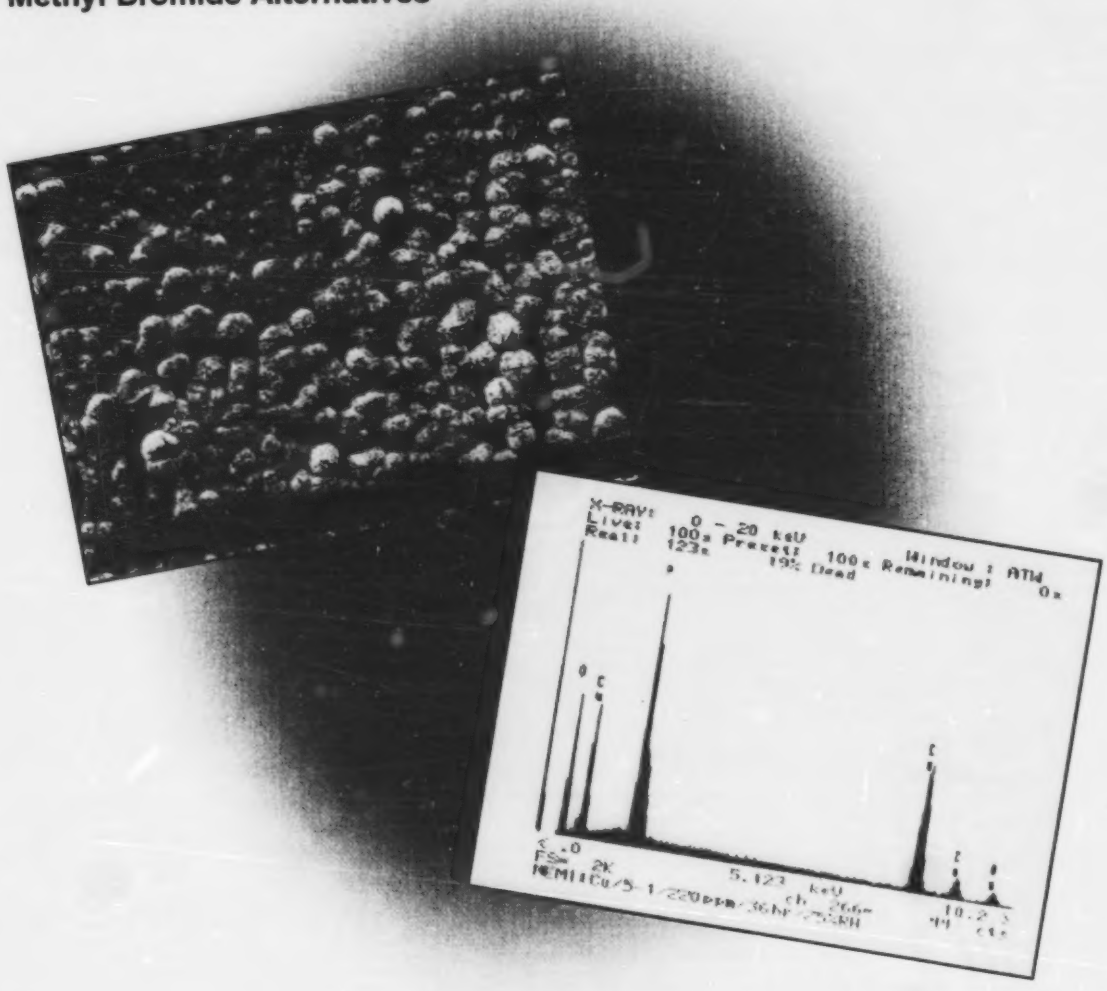
Corrosive Effects of Phosphine, Carbon Dioxide, Heat and Humidity on Electronic Equipment

Canada

Canadian Leadership in the Development of Methyl Bromide Alternatives



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101-04464/

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August 1998

Prepared for the:
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Agriculture and Agri-Food Canada
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and the Canadian National Millers Association

Acknowledgements

This study was sponsored by the United States Department of Agriculture, Agriculture and Agri-Food Canada, Environment Canada, Natural Resources Canada and the Canadian National Millers Association, with support from the Canadian food processing industry, the Canadian Pest Control Association and David Mueller of Fumigation Service and Supply, Inc., Indianapolis, IN, U.S.A. This project has been conducted under the auspices of the Canada/U.S. Working Group on Methyl Bromide Alternatives.

Graphic Design and Printing:
Bonanza Printing & Copying Centre Inc., Ottawa, ON

Printed in Canada on Recycled Paper.

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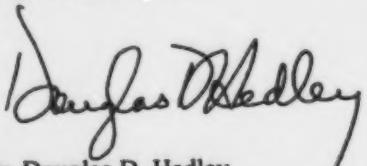
Foreword

The Montreal Protocol on Substances that Deplete the Ozone Layer is a global agreement intended to protect the ozone layer by reducing the production of ozone depleting substances. Developed countries that are signatory to the Montreal Protocol - this includes Canada and the United States - must completely phase-out the production and consumption of methyl bromide by the year 2005.

Controls on methyl bromide as an ozone depleting substance have resulted in a critical need for the development of alternatives for its use as a soil, commodity and structural fumigant. Through government research programs and commercial development of alternative technologies and products, we are making progress but more work is needed to ensure good control of pests and plant diseases in agriculture and food processing.

To maximize research collaboration and the development of alternatives, Agriculture and Agri-Food Canada (AAFC) and the United States Department of Agriculture (USDA) created an informal working group on methyl bromide alternatives. Agreement was reached to assist research scientists and industry to work together on common problems and projects and to share research results. Since a significant amount of methyl bromide is used in space fumigations for milling and food processing operations in Canada, and to a lesser extent in the United States, it was proposed that Canada lead this area within the working group. This report represents the second report of jointly funded collaboration between AAFC, USDA Agricultural Research Service scientists and private industry to develop methyl bromide alternatives.

This laboratory experiment also illustrates a key component of success in agri-food development. Research partnerships with industry and other government agencies are a cornerstone of AAFC's and USDA's programs. In this regard, the phosphine corrosion work could not have been conducted without the expertise of Dr. Robert Brigham of the Canada Centre for Mineral and Energy Technology (CANMET). Furthermore, we were pleased with the advice provided by the industry and, in particular, the insights of David Mueller (Fumigation Service & Supply Inc.) and his provision of corroded samples from field fumigations. The results of this laboratory experiment can easily be incorporated into field situations and will help to ensure effective pest control and reduce the risk of corrosion to electrical equipment by phosphine. We would like to express our thanks for the collaborative effort.



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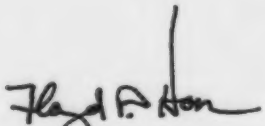

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EXECUTIVE SUMMARY

Four metals - silver (electrical contacts), copper (electrical conductors), brass (electrical components) and solder - were exposed to simulated fumigation parameters under carefully controlled steady-state laboratory conditions which included:

- three temperatures; 20, 30 and 40°C
- three concentrations of phosphine; nominally 35, 135 and 220 ppm
- four levels of relative humidity; 15, 25, 50 and 75%
- two levels of CO_2; nominally 3.5 to 5%
- three exposure times; 12, 24 and 36 hours

During the exposures, the phosphorus in phosphine was oxidized in the presence of water vapour to produce surface deposits of phosphorus oxides and the metals oxidized (corroded) in air at a rate controlled by the availability of oxygen to produce a weight gain. The corrosion products of metal oxidation (and the oxides of phosphorus) were removed to bare metal by immersion in 50/50 HCl and the resulting weight loss gave the corrosion rate of the metal.

The effects of surface roughness and carbon dioxide concentration were judged to be minimal so these kinetic data were lumped together in plotting the average effects of the other variables - relative humidity, temperature, phosphine concentration and exposure time.

The scanning electron microscope (SEM) with EDAX was used to observe the morphology and to determine the chemistry of surface deposits on the metallic coupons exposed in these experiments. The SEM was also used to reveal the morphology of corrosive attack of large copper strips which had been exposed at field fumigation sites. The typical morphology of corrosive attack of copper included areas with no attack, areas with general attack and areas with pits. Brass showed similar morphology to copper, but silver and solder were not attacked.

An unexpected result from this study concerned the identification of wet and dry regimes for copper exposed to phosphine as a function of relative humidity. Copper developed shiny black wet surface deposits only at low relative humidities (25% and lower); an observation which was both counter-intuitive and contradictory of anecdotal evidence. Dry crystalline surface deposits on copper were observed only at high relative humidities (50% and higher).

The table below summarizes the observations made in the course of this study on metal samples from a number of sources.

METAL	SOURCE	WEIGHT GAIN	CORROSION
Copper	This study Mueller samples	Extensive	Extensive
Nickel	Mueller calculator Mueller camera	Yes	?
Brass	This study	Yes	Yes
Silver	This study Mueller fumigation	Yes	No
Stainless Steel	Mueller camera	No P signature	None found
Solder	This study Mueller calculator Mueller fumigation	No	No

It should be noted that both surface deposits and corrosion morphology were identical whether produced in this study in the laboratory or in fumigations in the field.

Three possible failure mechanisms for electronic equipment exposed to phosphine have been identified:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals.

FIGURE CAPTIONS

Figure 1a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

Figure 1b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

Figure 2a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

Figure 2b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

Figure 3a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

Figure 3b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

Figure 4. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

Figure 5. EDAX spectrum of the surface deposits in Figure 4.

Figure 6a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 6b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 7a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

Figure 7b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

Figure 8a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

Figure 8b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

Figure 9. EDAX spectrum of the large black surface deposits in Figure 8a.

Figure 10. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 11. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 75% RH

Figure 12. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

Figure 13. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

Figure 14. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

Figure 15. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

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Figure 22. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

Figure 23. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

Figure 24. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

Figure 25. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

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Figure 27. Scanning electron micrograph (BSE mode) showing the extent of surface coverage of copper sample in Figure 6a (SE mode)

Figure 28. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

Figure 29. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

Figure 30. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

CORROSIVE EFFECTS OF PHOSPHINE, CARBON DIOXIDE, HEAT AND HUMIDITY ON ELECTRONIC EQUIPMENT

Introduction

The problem of metallic corrosion in phosphine has been addressed in early work in Canada(1) and more recent studies in Denmark(2) and the U.S.(3,4). However, the exposure conditions which promote attack and the corrosion mechanism are still not well understood. Consequently, this study was designed to quantify corrosion kinetics and morphology of metals commonly used in electronic equipment under carefully controlled laboratory conditions.

Four metals - silver (electrical contacts), copper (electrical conductors), brass (electrical components) and solder - were chosen for investigation. The materials were tested with both smooth surfaces and with abraded surfaces to increase the probability of water adsorption at a given relative humidity - a condition equivalent to having dust on the surface. It is believed that the corrosion behaviour of these four materials would indicate where corrosion problems with electrical components were likely to happen.

The grid of test parameters included:

- three temperatures; 20, 30 and 40°C
- three concentrations of phosphine; nominally 35, 135 and 220 ppm
- four levels of relative humidity; 15, 25, 50 and 75%
- two levels of CO_2; nominally 3.5 to 5%
- three exposure times; 12, 24 and 36 hours

Experimental

Conceptually, the experimental apparatus was designed to facilitate the manipulation of all the variables independently. To accomplish this, an air stream (1 litre/min) was saturated with water at low temperature in one Haake Model K constant temperature bath (to give 100% RH) and then the temperature of that stream was increased in a second Haake bath to the test temperature (20, 30 or 40°C) to give a lower pre-determined RH. In addition, CO_2 (from a cylinder of pure compressed gas) and PH_3 (from a N_2 - 0.5%PH_3 gas mixture purchased from Matheson) were bled into the second bath for pre-heating and mixing. This dilution lowered the RH in the carrier stream and that was adjusted by trial and error to the desired level as indicated by a VWR hygrometer. Gas flow rates were controlled by mass-flow meters and the resulting PH_3 concentration was monitored periodically throughout the 36-hour experiments with a PortaSens PH_3 meter. CO_2, air and N_2 flow rates were measured at the beginning and end of each experiment with soap-bubble flow meters and the long-term stability was found to be within the ±2% accuracy claimed by the manufacturer of the mass flow meters.

Each run was started by placing 8 weighed metallic samples with dimensions of approximately 50 x 13 x 0.1mm (surface area of 0.13 dm^2) in polyethylene cups with sides and top partially removed to allow free access and exit of the gas. Initial experiments were conducted with the samples mounted radially in the cups but in later runs with samples mounted parallel, the reproducibility seemed to improve. Copper (99.9%), brass (70/30 yellow brass shim stock), silver (99.9%) and solder (50/50 Pb-Sn) with as-rolled surfaces and surfaces abraded with 120 grit SiC were exposed. The samples were chemically cleaned in 50/50 HCl for 2 minutes before exposure. The cups containing the samples were placed in 3 chambers and the gas stream was routed to give exposures of 12, 24 and 36 hours. Steady state conditions of temperature and relative humidity as indicated by the digital hygrometer were achieved with a mixture of air, CO_2 and N_2. When the system had stabilized, the hygrometer was removed and a two-way valve was turned to replace the N_2 stream with the N_2 - 0.5% PH_3 mixture. Thereafter, bath temperatures and the PH_3 concentration were monitored regularly to ensure stability.

After each run, the samples were re-weighed in the as-removed condition, cleaned to bare metal by immersing in 50/50 HCl for 2 minutes and re-reweighed.

Results

a. Kinetics

During the exposures, the phosphorus in phosphine can be oxidized from the -3 valence state to higher oxidation states at metal surfaces in the presence of water vapour according to the following reactions(5):

- P oxidized from -3 to +1 (catalyzed by Cu, Ni, Pd, C)
  $PH_3 + 2H_2O = H_3PO_2 + 4H^+ + 4e^-$ (orthophosphorous acid)
- P oxidized from -3 to +3
  $PH_3 + 3H_2O = H_3PO_3 + 6H^+ + 6e^-$ (phosphorous acid)
- P oxidized from -3 to +5
  $PH_3 + 4H_2O = H_3PO_4 + 8H^+ + 8e^-$ (phosphoric acid)

These reactions result in surface deposits of phosphorus oxides and a weight gain. These weight gains are listed in the tables in Appendix A for copper, brass and silver but not for solder which did not gain weight under any exposure condition.

The tables of data also indicate that some samples were wet and others dry when removed. These observations are summarized below:

Metal	Temperature	15 & 25% RH	50 & 75% RH
Copper	all	wet	dry
Brass	40°C	wet	dry
	20 & 30°C	dry	dry
Silver	all	dry	wet
Solder	all	dry	dry

The behaviour of copper, ie. wet at low relative humidity and dry at high, is unexpected and counter-intuitive. On the other hand, silver showed the more expected wet/dry behaviour but the extent of wetting was minimal as indicated by the weight change. Wet silver samples were merely cloudy to the naked eye and under the low-power stereo microscope, small "dew drops" covered the surface. Brass behaviour was intermediate between copper and silver with the low relative humidity wetting characteristic of copper observed only at 40°C. Solder showed no weight gain and no P signature with energy dispersive analysis by x-rays (EDAX) under any test condition.

Copper, brass and silver are thermodynamically stable in non-oxidizing acid solutions and, consequently, do not corrode in these solutions. However, they do oxidize (corrode) in air at a rate controlled by the availability of oxygen and any tendency to passivate is prevented by low pH solution. The corrosion products of metal oxidation (and the oxides of phosphorus deposited in the above reactions) can be removed to bare metal by immersion in 50/50 HCl, a non-oxidizing acid, and the resulting weight loss gives the corrosion rate of the metal. Weight losses after stripping to bare metal are also given in Appendix A.

b. Morphology

The scanning electron microscope (SEM) with EDAX was used to observe the morphology and to determine the chemistry of surface deposits on the metallic coupons exposed in these experiments. Because the surface deposits were electrically non-conducting, a thin evaporated gold coating was applied to minimize charging in the electron beam. The SEM was also used to reveal the morphology of corrosive attack on coupons after chemical cleaning with HCl. The same techniques were used to evaluate the morphology of large copper strips which had been exposed at fumigation sites by Fumigation Service and Supply, Inc.

Figures 1a, 2a and 3a show the typical morphology of surface deposits in the back- scattered electron(BSE) mode on copper (the dry regime) and Figures 1b, 2b and 3b how the progression of corrosive attack including areas with no attack, areas with general attack and areas with pits on the same samples after chemical cleaning to bare metal. The BSE mode clearly distinguishes between relatively bare metal where electrons are back-scattered efficiently and the area appears bright and coated areas which appear dark. Figure 4 reveals the morphology of Figure 3a more clearly in the secondary electron (SE) mode and it is clear that the surface after 36 hours is almost completely covered with small nodules. The EDAX spectrum in Figure 5 shows only P, O and Cu (H cannot be detected using EDAX).

The dry morphology shown in Figures 1, 2 and 3 can be contrasted with the morphology of the wet regime shown in Figures 6a, 7a and 8a (SE mode) for copper after 12, 24 and 36 hours at 40°C, 220 ppm PH_3 and 15% RH. The extent of corrosion on the same samples is shown in Figures 6b, 7b and 8b after chemical cleaning in the same way as samples in Figures 1b, 2b and 3b. At 40°C, the coating material is more resistant to the 50/50 HCl cleaning solution and a certain amount of residue remains in some pits (see Figure 8b). Although the surface coating formed on copper at 40°C is more resistant to dissolution, the EDAX spectrum in Figure 9 shows it to be chemically similar to the coating formed at 30°C (see Figure 5).

The wet and dry morphologies observed on brass were similar to those discussed above for copper but in the case of silver, the extent of surface coverage was minimal. Figure 10 shows the very limited extent of coverage on silver exposed for 12 hours at 40°C to 220 ppm PH_3 (dry regime for silver) and Figure 11 shows the increased, but still small, coverage at 75% RH (wet regime). No corrosion was found on chemically cleaned silver coupons.

In addition to laboratory coupons, the following observations have been made with respect to copper samples exposed in field fumigations(3,4)

- surface deposits on the copper are mainly colourless to slightly bluish crystals. A few random dark circular deposits seem to be associated with surface dust.
- these deposits are not electrical conductors and charge in the electron beam of the SEM.
- EDAX shows that the elements present are Cu, P and O.
- surface deposits nucleate at surface imperfections such as rolling marks and grow rapidly to increase surface coverage but in a non-linear way
- when the surface deposits were removed in 50/50 HCl, the copper substrate showed areas of no attack, areas of general attack and other areas with pitting.

Discussion

Because single coupons of each metal were exposed under each of the steady-state exposure conditions, the weight change data in Appendix A are characterized by considerable scatter and are not amenable to statistical analysis. However, a number of interesting trends are discussed below.

Effect of Surface Roughness

In Appendix A, any differences in weight change between smooth samples and samples abraded with 120 grit SiC paper seemed to be minimal and within the sample to sample scatter in the data. Consequently, the data for smooth and rough samples were averaged for trend analysis.

Effect of Carbon Dioxide Concentration

Differences in CO_2 concentrations (3.2% vs. 4.5% and 3.5% vs. 5.0%) had minimal effect on weight change data and results at high and low CO_2 were averaged for trend analysis. If CO_2 has an effect, it may be a small one in defining equilibrium conditions for wet/dry morphology - see for example the behaviour of brass in 220 ppm PH_3 at 40°C and 25% RH in 3.5 vs. 5% CO_2 (Appendix A).

Effect of Relative Humidity

Copper is clearly a special case where the effect of relative humidity on weight gain is entirely counter-intuitive. At 15 and 25% relative humidity, copper coupons were observed to be wet after exposure whereas at the higher humidity levels investigated - 50 and 75% RH - the copper samples were invariably dry and coated with crystalline material. In Figure 12, the average weight change

of smooth and rough copper coupons exposed to 3.5 and 5% CO_2 and 220 ppm PH_3 for 36 hours is plotted as a function of RH for the 3 exposure temperatures. The effect of wetness on weight gain is apparent at 40 and 30°C but not at 20°C. Wetness had only a minimal effect on weight loss (corrosion) as might be expected in the case were corrosion rate is controlled by oxygen availability.

For brass weight change results averaged in the same way and shown in Figure 13, it should be noted that wetness was observed only at lower relative humidities and only at 40°C. This was the case at lower PH_3 concentrations as well. As with the copper, weight loss (corrosion) was relatively unaffected by wetness and the corrosion rates of copper and brass were similar under most conditions as would be expected where oxygen availability controlled. Weight gains, however, were consistently lower on brass than on copper.

As shown in Figure 14, the data for silver (averaged in the same way as for copper and brass above) reflects the intuitive relationship of increasing weight change with increasing RH and, indeed, small droplets of moisture were observed at higher relative humidities. Based on the minute weight losses and morphological observations, it can be concluded that silver does not corrode in phosphine.

Effect of Temperature

An example of the effect of temperature on reaction kinetics is shown in Figure 15 for copper. In the wet regime (15 and 25% RH), increasing temperature has a significant effect on both weight gain and weight loss kinetics. In the dry regime (50 and 75% RH), only the highest temperature (40°C) leads to significant increases in reaction rates.

Unlike copper, brass (shown in Figure 16) is dry at low relative humidities (15 and 25%) and low temperatures (20 and 30°C) and shows no temperature dependence in this range. With the onset of the wet regime at 40°C, kinetics increase dramatically at 25% RH but are much more muted at 15%.

The weight gain kinetics of silver shown in Figure 17 are greatly accelerated with increasing temperature at all relative humidity levels but the absolute values are very small relative to copper and brass under the same conditions. Silver does not corrode in the temperature range 20 to 40°C.

Effect of Phosphine Concentration

In general, weight changes of copper, brass and silver vary in a linear way with increasing PH_3 concentrations. For example, Figures 18, 19 and 20 show the weight gains and weight losses on copper at 20, 30 and 40°C, respectively, with changes in PH_3 concentration from 35 to 220 ppm. At 35 ppm PH_3, the weight changes are essentially zero (<0.7mg in 36 hours) at all temperatures but change dramatically as PH_3 increases to 220 ppm. In the dry regime (50 and 75% RH), the weight increase appears to be linear while in the wet regime (15 and 25% RH) the increase is somewhat erratic but the trend is clearly upward and strongly temperature dependent. Weight losses

(corrosion) of copper also increase with PH_3 concentration but are insensitive to wet/dry variations except at the lowest temperature. The behaviour of brass parallels that of copper as shown in Figures 21 and 22 at 30 and 40°C, respectively, but with smaller overall weight changes.

Silver at 30°C (Figure 23) experiences minimal weight increases (<1mg in 36 hours) and is relatively insensitive to PH_3 concentration but at 40°C (Figure 24) the weight gain trends are similar to copper and brass. The corrosion rate of silver can be taken as zero at all PH_3 concentrations and temperatures.

Effect of Exposure Time

Reaction kinetics of metals in PH_3 as measured by weight change has been observed to be linear with time or to accelerate with time. Accelerating weight increase is consistent with nucleation at points on the surface, grow of these deposits with time leading to complete surface coverage and subsequent linear kinetics. This kind of behaviour is evident in Figures 1a, 2a and 3a for copper at 30°C. The related kinetics in Figure 25 show the weight change accelerating with time. However, at 40°C, Figure 26, the kinetics become linear after 12 hours; the time required for extensive surface coverage as shown in Figure 27, the BSE image which shows surface coverage more clearly than the SE image in Figure 6a.

On the other hand, as shown in Figure 28, brass kinetics are linear at 30°C (dry regime) because the degree of surface coverage remains low even after 36 hours. However, brass kinetics accelerate at 40°C as shown in Figure 29, particularly in the wet regime, where surface coverage approaches 100% after 36 hours.

The kinetics for silver are essentially linear with time and very slow relative to brass and copper consistent with the minimal surface coverage even after 36 hours of exposure. An example of silver at 40°C is shown in Figure 30. Silver does not corrode as indicated by both weight-loss results and SEM observations.

The weight changes plotted above can be converted into corrosion rates. For copper, a weight change of 1mg in 24 hours on a sample with an area of $0.13dm_2$ produces a rate of 7.7mdd (milligrams per square decimeter per day) or a penetration rate (on a planar interface) of 0.03mm/year (0.0012 inches per year). Consequently, if the weight-loss data plotted in Figures 25 (30°C) and 26 (40°C) at each time are averaged, the following rates can be calculated for copper exposed to 220 ppm PH_3:

EXPOSURE TIME (hrs)	RATE at 30°C (mdd)	RATE at 30°C (mm/yr)	RATE at 40°C (mdd)	RATE at 40°C (mm/yr)
12	18	0.7	52	2
24	27	1	62	2.4
36	29	1.1	65	2.5

As noted above, increasing rates are consistent with a mechanism involving nucleation at points on the surface followed by growth with time until complete surface coverage when rates become

constant. Constant rates are reached more quickly at 40°C than at 30°C because of the faster kinetics at higher temperature.

Comments on Morphology

Nucleation and growth of surface deposits has been observed in all cases but the size of deposits varies considerably depending on whether the steady-state conditions produce wet or dry behaviour. With copper, for example, nodules approximately 50μ in diameter were observed in the dry regime (see Figure 4) but in the wet regime, large black blobs up to 1mm in diameter were formed after 36 hours(see Figure 8a). On a macroscopic scale, copper samples appeared black and shiny in the wet regime and only dulled in the dry regime.

Summary

Within the envelope of variables studied (20 to 40°C, 35 to 220 ppm PH_3, 15 to 75% RH), it is now clear that electronic equipment exposed to phosphine fumigations might fail by any of three mechanisms:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals.

The only failed electronic component examined in this laboratory was a switch supplied by Michelle Marcotte (6) in which the first possible mechanism - the build-up of non-conducting compounds rich in P and O - had occurred on the silver contacts. Reports of other failures in the field have been anecdotal and have suggested that high relative humidity was the primary factor which should be avoided - a conclusion not supported by this study.

The table below summarizes the observations made in this course of this study on metal samples from a number of sources.

METAL	SOURCE	WEIGHT GAIN	CORROSION
Copper	This study Mueller samples	Extensive	Extensive
Nickel	Mueller calculator Mueller camera	Yes	?
Brass	This study	Yes	Yes
Silver	This study Mueller fumigation	Yes	No
Stainless Steel	Mueller camera	No P signature	None found
Solder	This study Mueller calculator Mueller fumigation	No	No

It should be noted that both surface deposits and corrosion morphology were identical whether produced in this study in the laboratory or in fumigations in the field.

Conclusions

1. Within the grid of test parameters, the steady-state technique used in this study which facilitates the variation in all the parameters independently has clarified in a global sense the relative severity of metallic "corrosion" in phosphine by quantifying the extent of both surface deposit formation and metallic dissolution of the metals studied.

2. The most significant results from this study concern the identification of wet and dry regimes for copper as a function of relative humidity. Copper develops shiny black wet surface deposits only at low relative humidities (25% and lower); an observation which is both counter-intuitive and contradictory of anecdotal evidence. Dry crystalline surface deposits on copper are observed only at high relative humidities (50% and higher).

3. Different metals behave differently when exposed to phosphine in terms of wet/dry regimes and overall reaction rates. Copper, and to a lesser extent brass, develop massive wet surface coatings at low relative humidity whereas silver becomes slightly wet at high relative humidities. Copper, and to a lesser extent brass, form surface deposits and suffer pitting and general corrosion. Silver develops surface deposits but does not corrode. Solder is inert.

4. Three possible failure mechanisms for electronic equipment exposed to phospine have been identified:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals.

Recommendations

This study has made significant progress in clarifying in a global sense the relative severity of metallic "corrosion" in phosphine but the following additional work might be considered:

1. Additions to the existing data base.

   Additional work is required to define more closely the relative humidity in the range 25 to 50% at which copper changes from the wet to dry regime. This work would be done at different phosphine levels, possibly 85 and 180 ppm and even one very high level >220 ppm, to expand the data base rather than duplicate existing information. It is clear that any additional work should include replicate samples of copper for subsequent statistical analysis and nickel, a common component of circuit boards on which oxides of phosphorus have been observed after field fumigations, should be included in the study. Data at 0% carbon dioxide may be of interest to some.

2. Inducing failures in electronic equipment.

   A number of possible failure mechanisms have been identified but, with the exception of one switch with silver terminals, no failed electronic components have been examined. The experimental parameters which are believed to be most aggressive have been identified and the experimental feasibility of carrying out long-term steady state exposures has been

demonstrated. Therefore, it is now possible to induce failures in small electronic components and carry out failure analyses to identify precisely the conditions to be avoided.

3. Evaluating of the effects of cyclical exposure parameters.

Work to date has been performed under steady-state conditions but it is possible to cycle independently the temperature, relative humidity, PH_3 concentration and CO_2 concentration to more closely duplicate the conditions of field fumigations. The effect of repeated exposures might also be of practical interest to the industry.

4. Understanding the chemistry of phosphine in contact with metals.

The chemistry invovled in the wet/dry transition of copper exposed to phosphine is clearly not understood and is of great theoretical interest. Analytical equipment now exists which could clarify the reactions involved.

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2. Ebbe Rislund, Corrosion Aspects of Phosphine Fumigation, Danish Environmental Protection Agency Arbejasrapport Tra Miljostyrelsen, Working Report No. 29 (1996)
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6. Michelle Marcotte, private communication

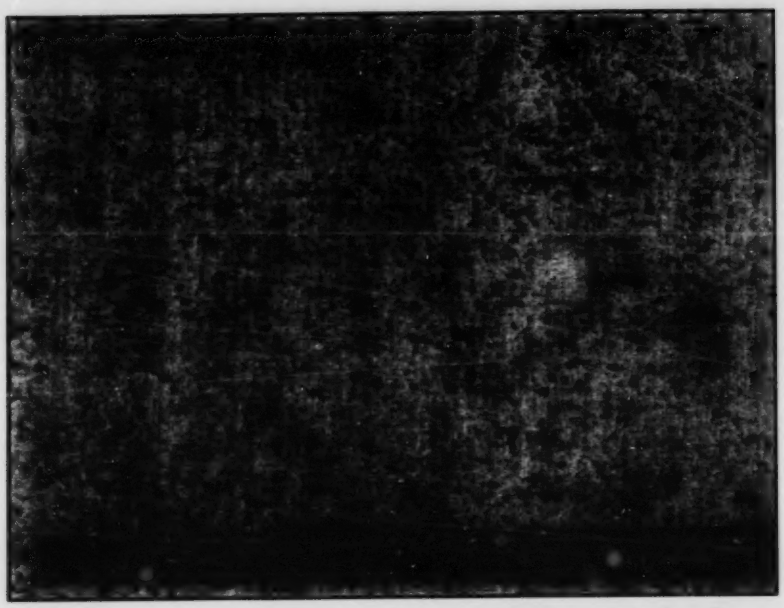


Figure 1a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

Figure 1b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

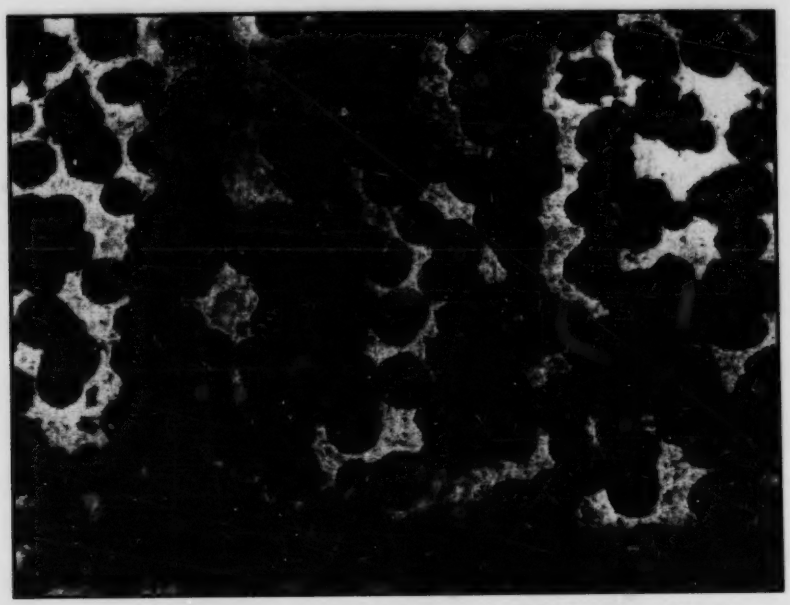


Figure 2a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

Figure 2b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

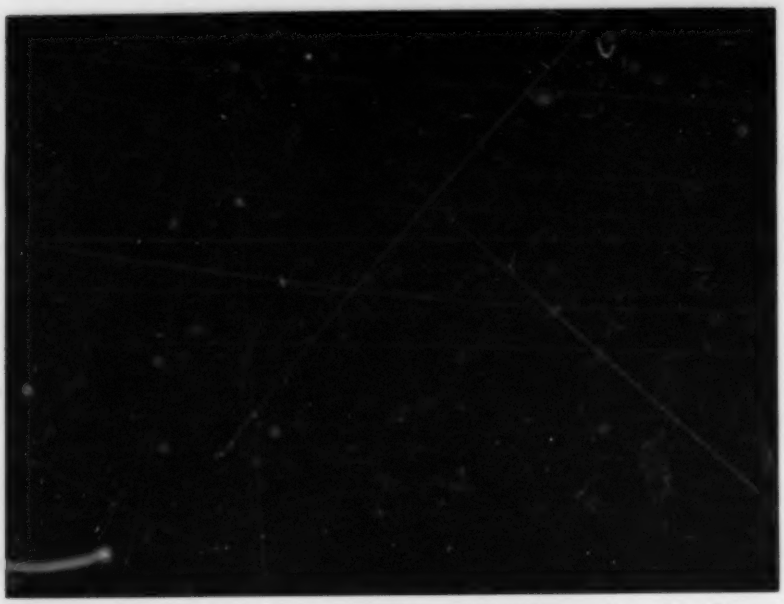


Figure 3a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

Figure 3b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

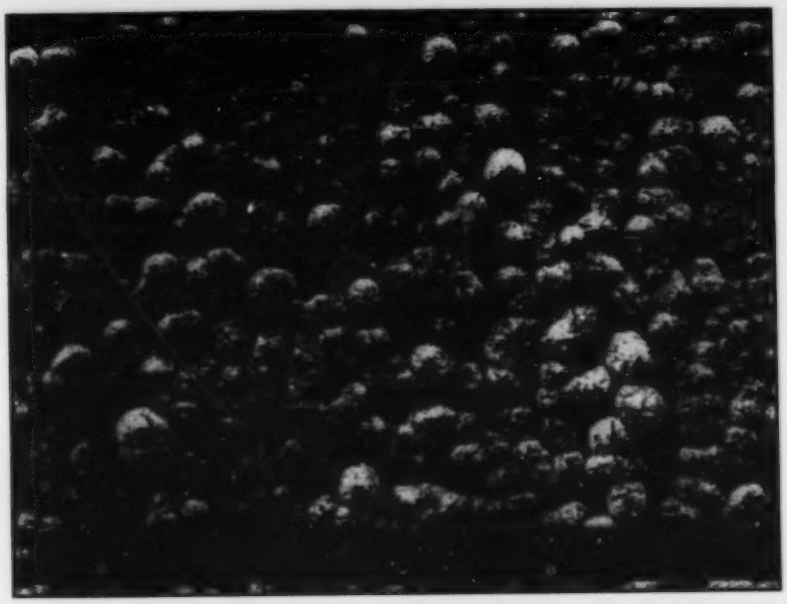


Figure 4. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

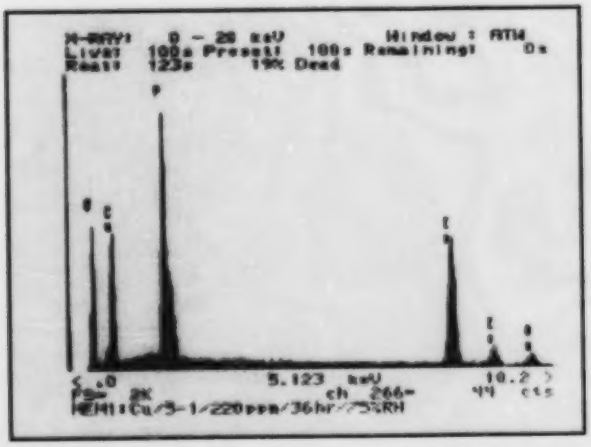


Figure 5. EDAX spectrum of the surface deposits in Figure 4.

Figure 6a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 6b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 7a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

Figure 7b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

Figure 8a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

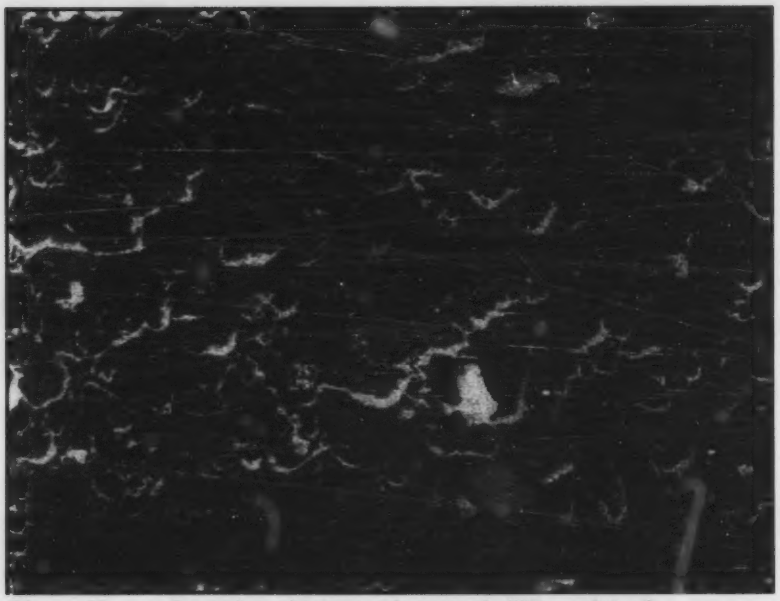


Figure 8b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

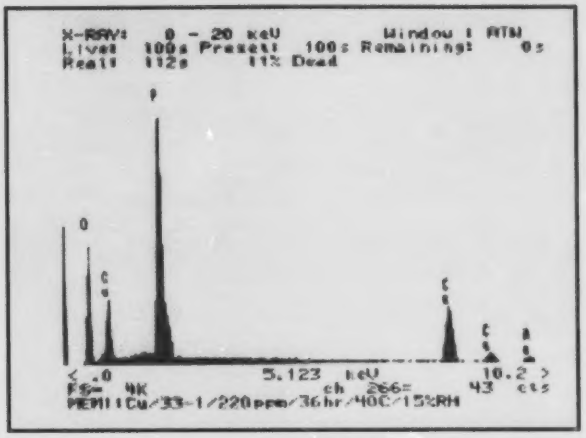


Figure 9. EDAX spectrum of the large black surface deposits in Figure 8a.

Figure 10. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

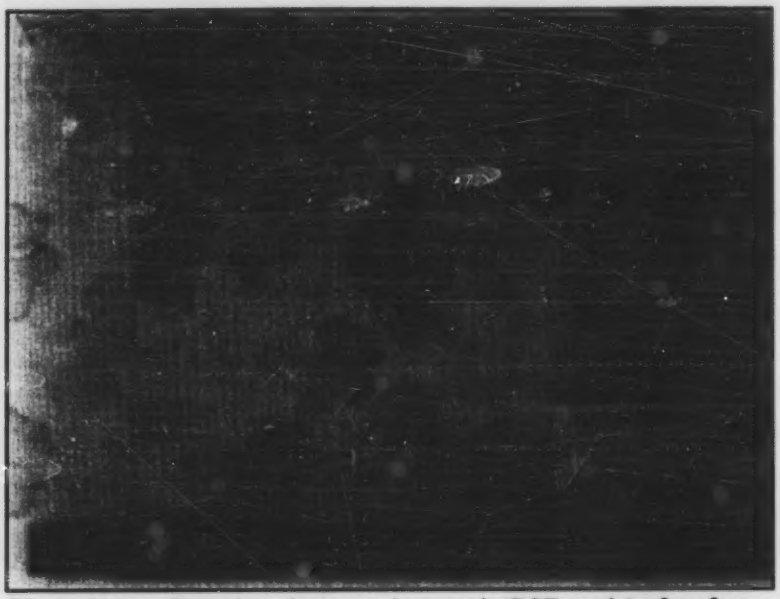


Figure 11. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 75% RH

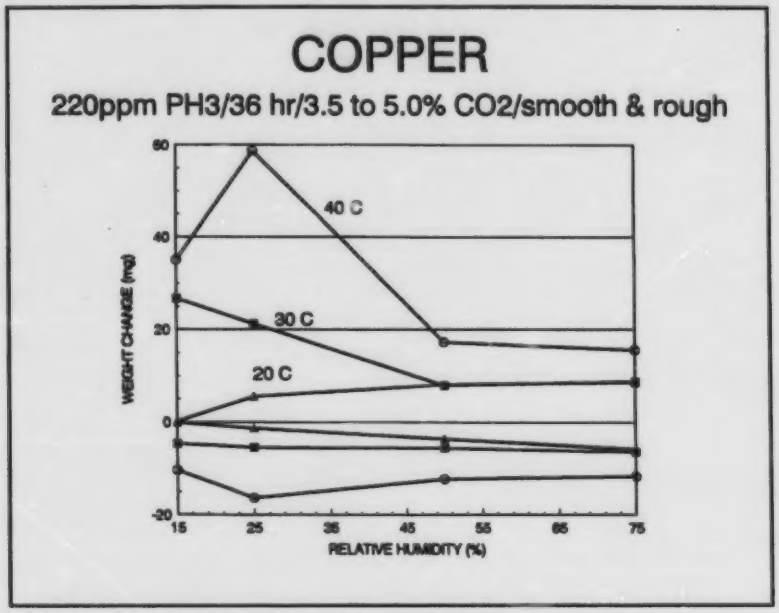


Figure 12. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

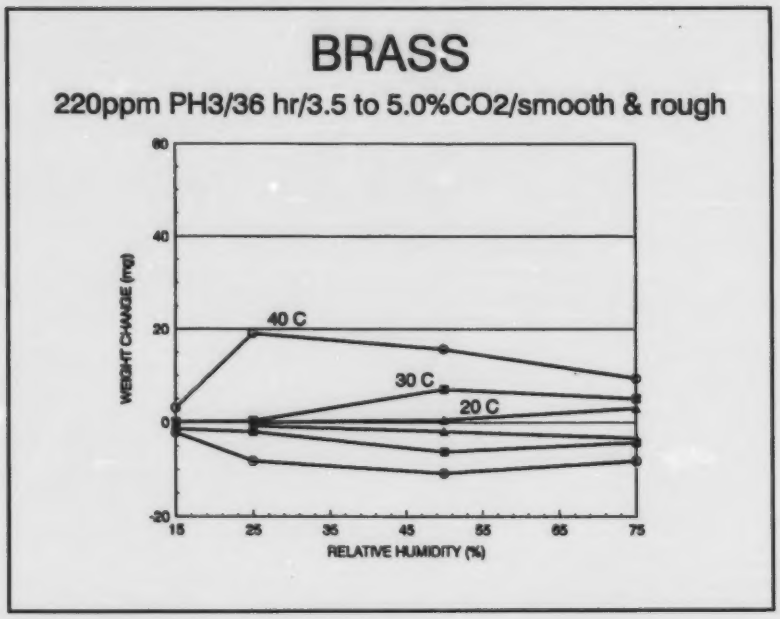


Figure 13. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

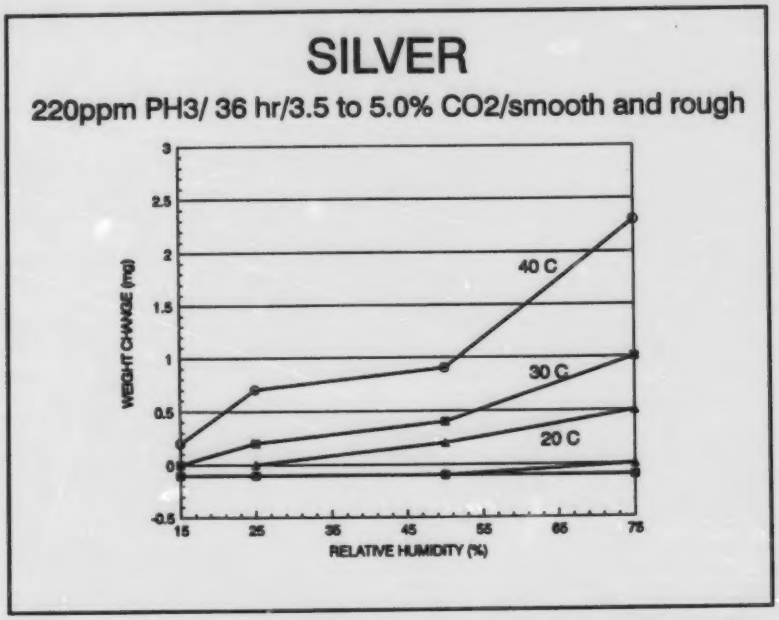


Figure 14. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

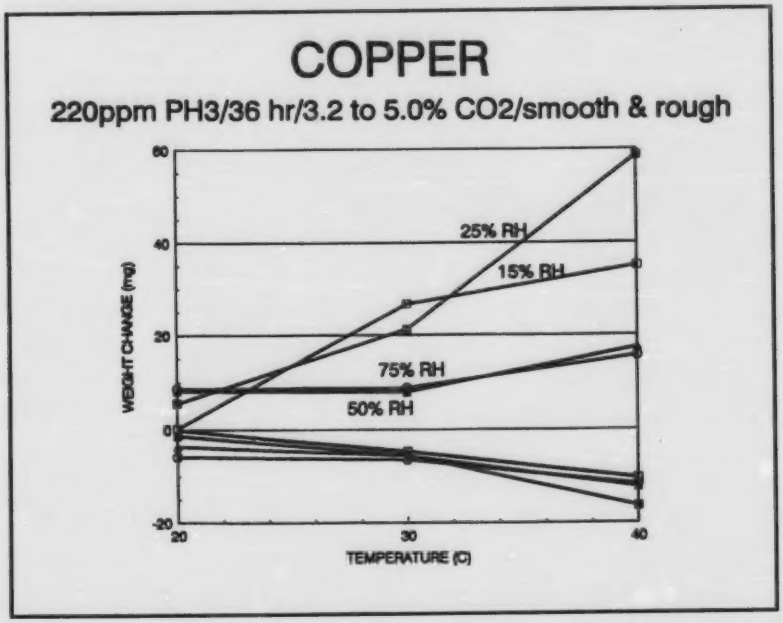


Figure 15. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

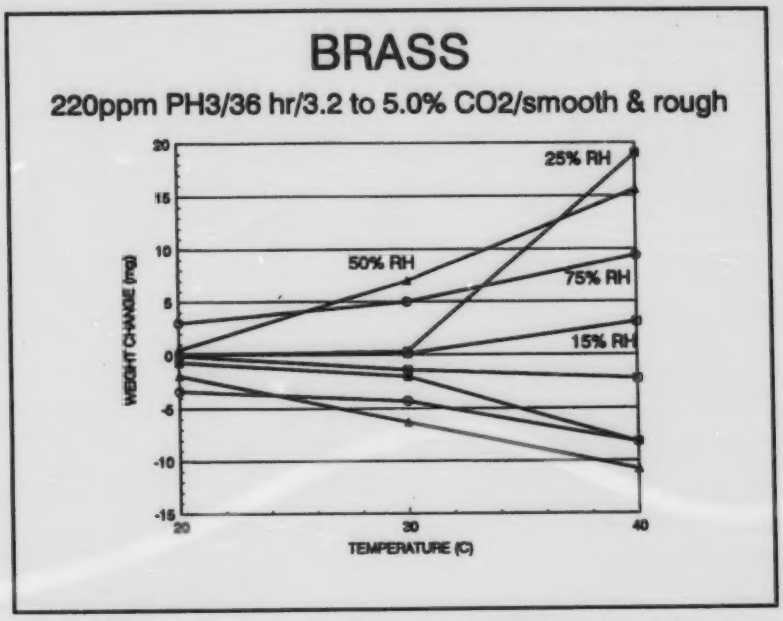


Figure 16. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

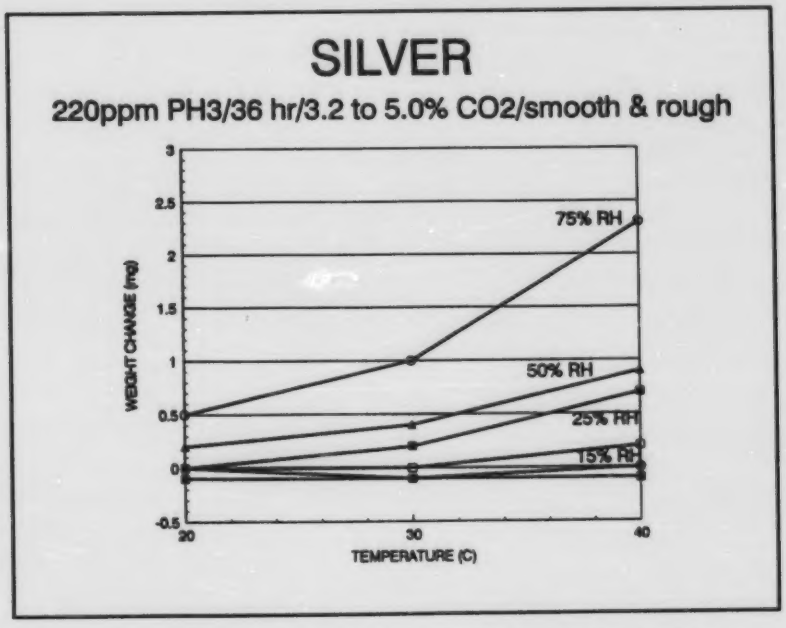


Figure 17. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

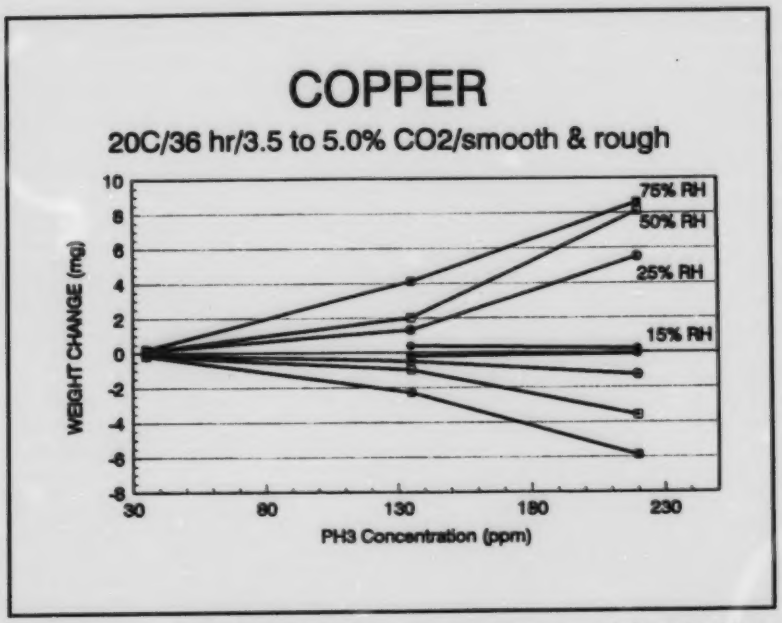


Figure 18. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

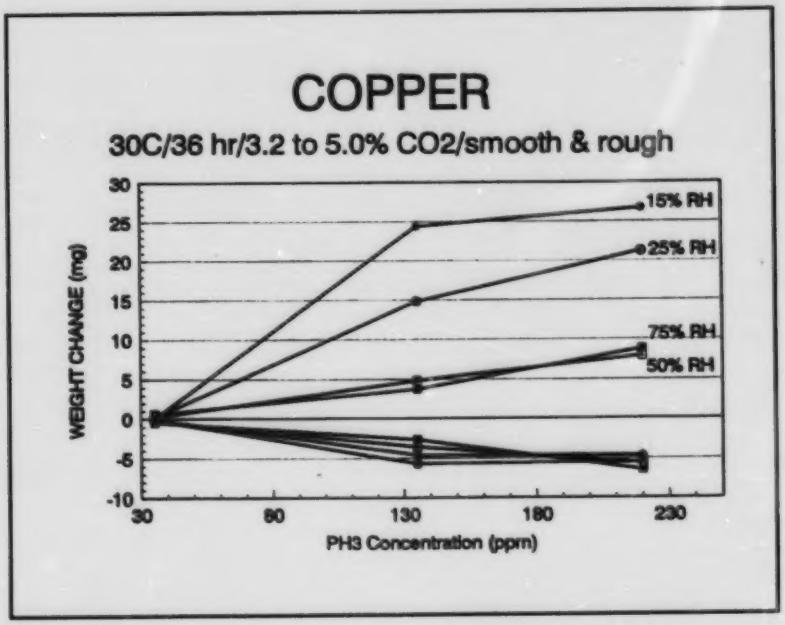


Figure 19. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

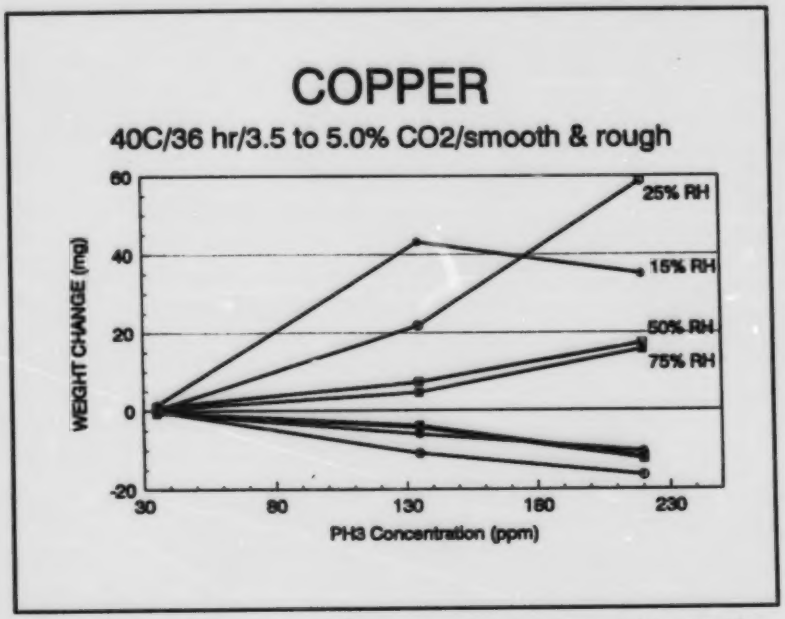


Figure 20. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

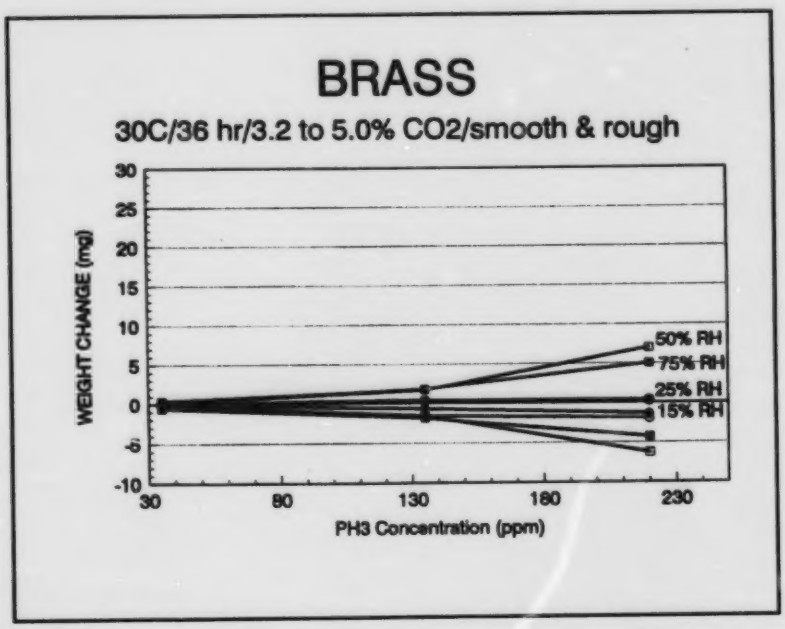


Figure 21. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

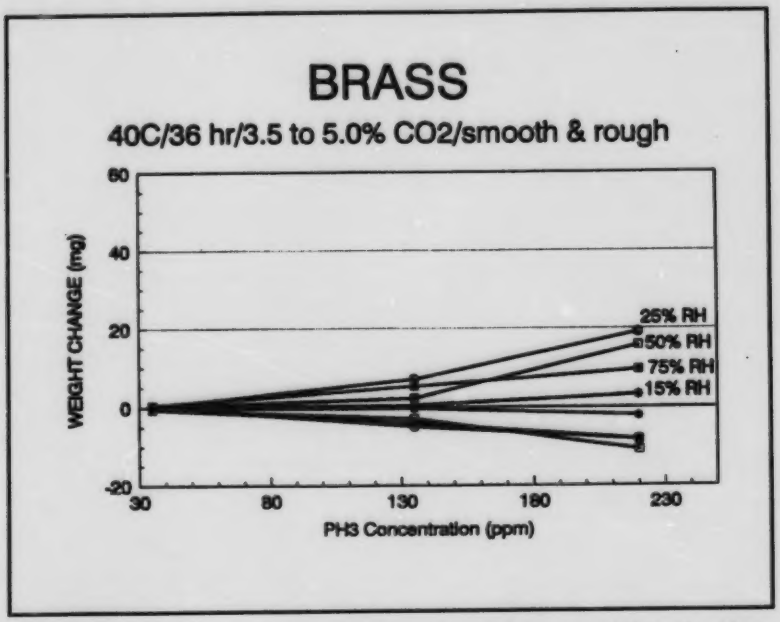


Figure 22. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

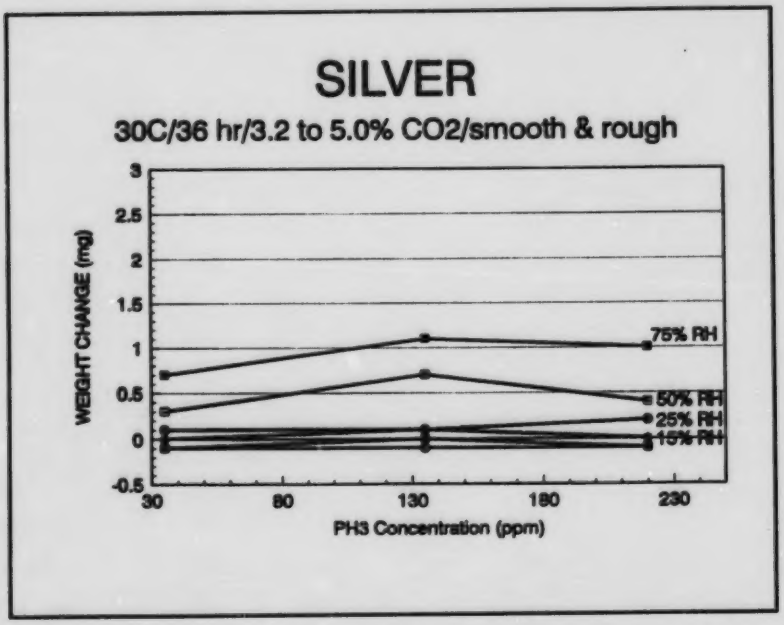


Figure 23. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

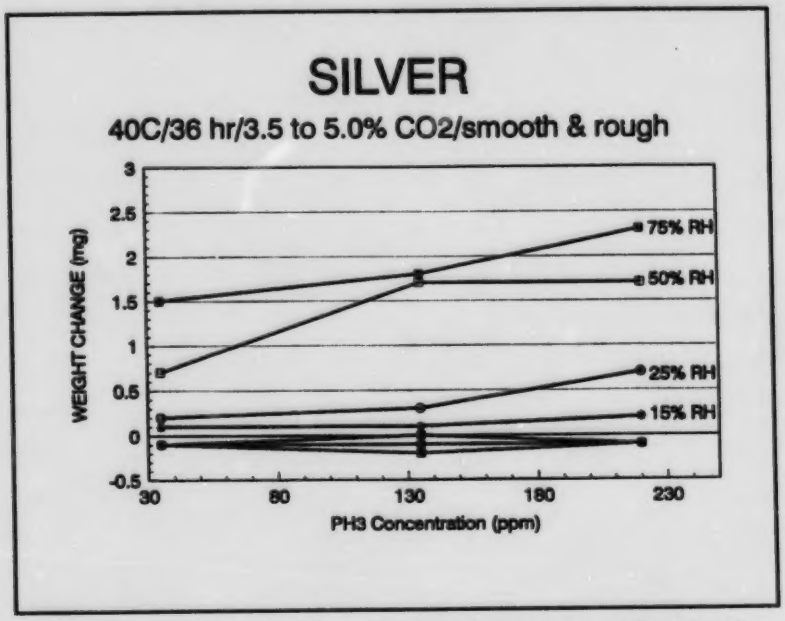


Figure 24. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

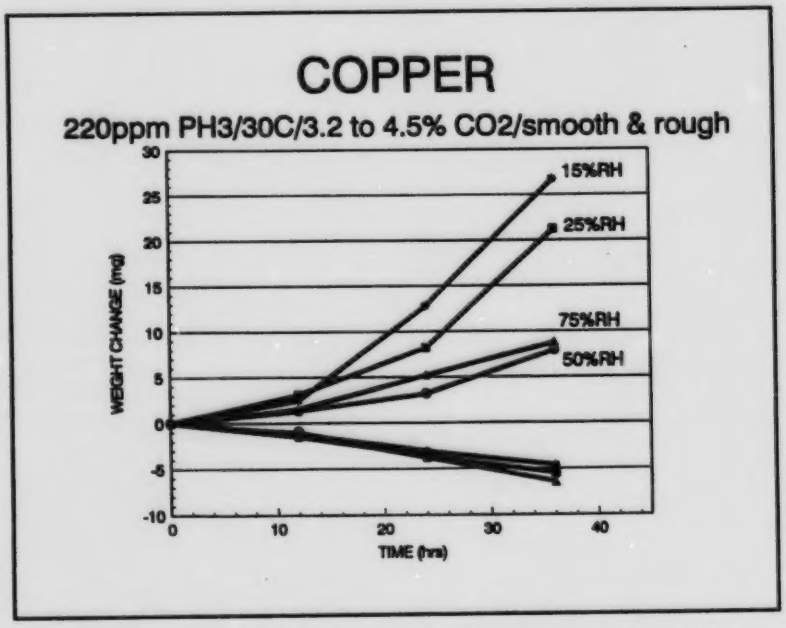


Figure 25. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

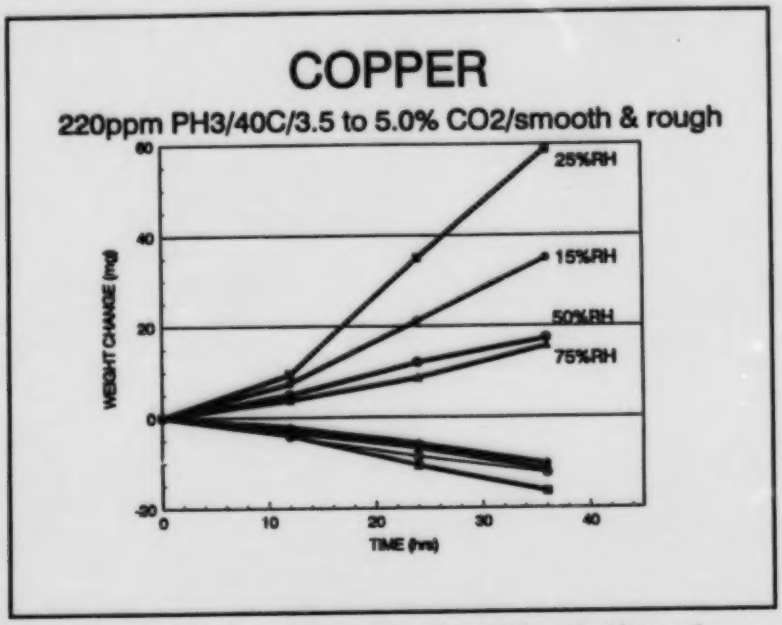


Figure 26. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

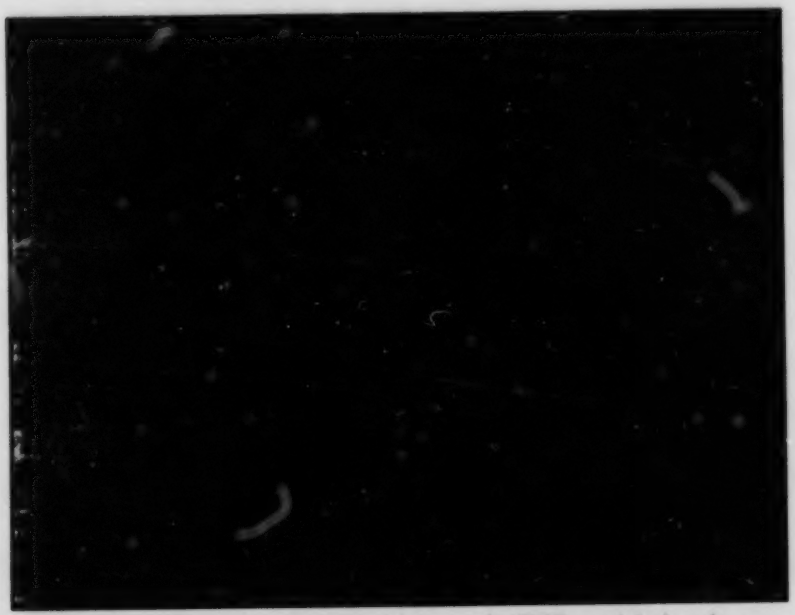


Figure 27. Scanning electron micrograph (BSE mode) showing the extent of surface coverage of copper sample in Figure 6a (SE mode)

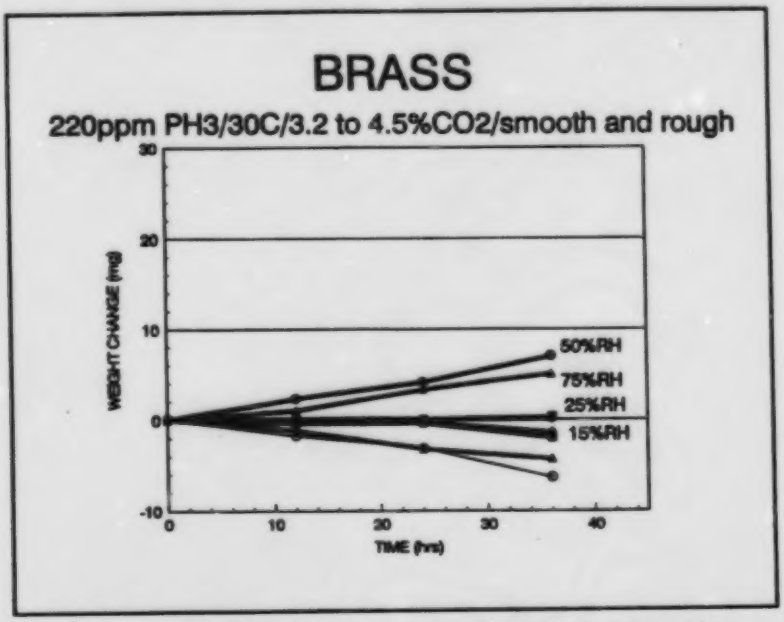


Figure 28. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

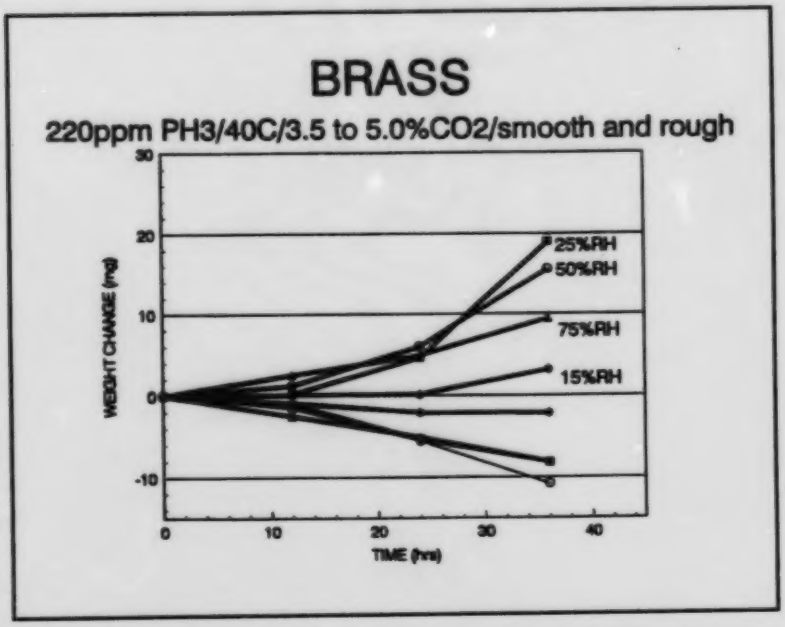


Figure 29. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

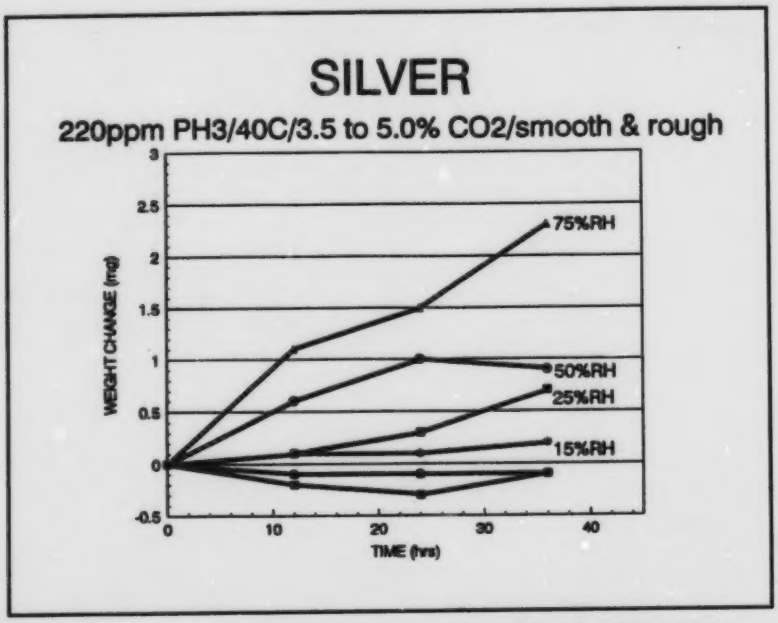


Figure 30. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

APPENDIX A

Tables of weight gain and weight loss are compiled in Appendix A for the following experimental parameters:

20°C, 5.0% CO_2, 35 ppm PH_3
20°C, 5.0% CO_2, 135 ppm PH_3
20°C, 3.5% CO_2, 220 ppm PH_3
20°C, 5.0% CO_2, 220 ppm PH_3

30°C, 5.0% CO_2, 35 ppm PH_3
30°C, 3.2% CO_2, 135 ppm PH_3
30°C, 5.0% CO_2, 135 ppm PH_3
30°C, 3.2% CO_2, 220 ppm PH_3
30°C, 4.5% CO_2, 220 ppm PH_3

40°C, 5.0% CO_2, 35 ppm PH_3
40°C, 5.0% CO_2, 135 ppm PH_3
40°C, 3.5% CO_2, 220 ppm PH_3
40°C, 5.0% CO_2, 220 ppm PH_3

20C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	-	-	XX	0.1	-	0.1
		24 hr	XX	-	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	-	0.2	XX	-	0.1	0.1
	Rough	12 hr	XX	-	-	-	XX	0.1	0.1	0.2
		24 hr	XX	-	-	0.1	XX	0.2	0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.2	0.2	0.2
Brass	Smooth	12 hr	XX	0.1	-	-	XX	-	0.1	0.1
		24 hr	XX	0.1	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.1	0.1	0.2
	Rough	12 hr	XX	-	-	-	XX		0.2	0.2
		24 hr	XX	-	-	0.1	XX		0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX		0.2	0.3
Silver	Smooth	12 hr	XX	-	-	-	XX	-	-	-
		24 hr	XX	-	-	-	XX	-	-	-
		36 hr	XX	-	-	0.1	XX	-	-	-
	Rough	12 hr	XX	-	-	-	XX	0.2	0.3	0.2
		24 hr	XX	-	-	-	XX	0.2	0.2	0.2
		36 hr	XX	-	0.1	-	XX	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
All samples mounted parallel

20C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.3	0.8	-	-	0.2	0.5
		24 hr	-	0.1	0.6	2.1	-	0.1	0.3	1.4
		36 hr	0.2	0.7*	1.5	4.2	0.1	0.3	0.8	2.2
	Rough	12 hr	-	-	0.3	0.9	0.1	0.2	0.3	0.6
		24 hr	0.1	0.3	0.9	2.3	0.1	0.3	0.5	1.4
		36 hr	0.6	1.8	2.5	3.9	0.2	0.6	1.2	2.4
Brass	Smooth	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.5
		24 hr	-	-	0.1	0.7	0.1	0.1	0.3	1.0
		36 hr	-	0.1	0.4	1.2	0.1	0.3	0.8	1.9
	Rough	12 hr	-	-	-	0.2	0.2	0.2	0.3	0.5
		24 hr	-	-	-	0.3	0.2	0.3	0.3	1.0
		36 hr	-	-	0.1	0.6	0.2	0.3	0.6	1.5
Silver	Smooth	12 hr	-	-	-	-	-	-	-	-
		24 hr	-	-	-	-	-	-	-	0.1
		36 hr	-	-	0.1	0.3*	-	-	-	-
	Rough	12 hr	-	-	-	0.1	0.2	0.2	0.2	0.1
		24 hr	-	-	0.1	0.1	0.1	0.3	0.2	0.2
		36 hr	-	-	0.1	0.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

20C/220 ppm PH_3/3.5% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	1.2	1.8	XX	-	0.7	1.3
		24 hr	XX	0.4	3.2	4.6	XX	0.1	1.7	3.3
		36 hr	XX	4.4*	6.5	6.4	XX	1.2	2.8	4.7
	Rough	12 hr	XX	0.2	2.1	2.2	XX	0.2	1.6	1.4
		24 hr	XX	0.9	4.6	5.9	XX	0.3	2.2	3.2
		36 hr	XX	7.2*	10.9	10.7	XX	1.6	4.6	6.6
Brass	Smooth	12 hr	XX	-	0.3	1.1	XX	0.1	0.3	1.0
		24 hr	XX	-	0.4	1.3	XX	0.2	0.3	2.0
		36 hr	XX	-	0.9	4.5	XX	0.8	2.0	3.9
	Rough	12 hr	XX	-	-	0.2	XX	0.2	0.4	0.7
		24 hr	XX	-	-	0.2	XX	0.3	1.3	1.3
		36 hr	XX	0.1	-	1.7	XX	0.6	2.0	2.4
Silver	Smooth	12 hr	XX	-	0.1	0.1	XX	-	-	-
		24 hr	XX	-	0.1	0.2	XX	-	-	-
		36 hr	XX	-	0.2	0.4	XX	-	-	-
	Rough	12 hr	XX	-	-	0.1	XX	0.3	0.2	0.1
		24 hr	XX	-	0.1	0.2	XX	0.2	0.2	0.1
		36 hr	XX	0.1	-	0.3	XX	0.1	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

20C/220 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.5	1.2	-	-	0.3	0.9
		24 hr	0.1	0.3	2.4	4.1	-	0.2	1.1	2.6
		36 hr	0.2	4.4*	6.1	5.1	-	1.1	3.1	5.1
	Rough	12 hr	0.1	0.1	0.6	1.7	0.1	0.1	0.4	1.0
		24 hr	0.1	0.6	4.1	6.7	0.1	0.2	1.6	3.9
		36 hr	0.2	6.1*	8.9	12.0	0.1	1.2	4.0	7.0
Brass	Smooth	12 hr	-	0.1	-	0.7	-	-	0.2	0.8
		24 hr	-	-	0.1	1.7	-	0.1	0.8	2.2
		36 hr	0.1	-	1.1	4.5	-	0.8	2.0	4.3
	Rough	12 hr	-	-	-	0.4	0.2	0.2	0.4	0.8
		24 hr	-	-	-	0.2	0.2	0.2	0.9	1.3
		36 hr	-	-	0.1	1.4	0.2	0.7	1.6	2.8
Silver	Smooth	12 hr	-	-	-	0.1	-	-	0.1	0.1
		24 hr	-	-	0.3*	0.2	-	-	-	-
		36 hr	-	-	0.4*	0.6	-	-	-	-
	Rough	12 hr	-	-	0.3	0.3	0.2	0.3	0.1	0.2
		24 hr	-	-	0.1	-	0.2	0.2	0.2	0.3
		36 hr	-	-	0.2	0.7	0.2	0.3	-	-

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	-	-	0.2	0.1	0.1	0.1	0.1
		24 hr	-	-	0.2	0.2	-	0.1	0.2	0.2
		36 hr	-	0.1	0.3	0.6	-	0.1	0.3	0.5
	Rough	12 hr	-	-	-	0.2	0.1	0.1	0.2	0.3
		24 hr	-	0.2	0.2	0.2	0.2	0.1	0.1	0.2
		36 hr	0.1	0.2	0.1	0.5	0.1	0.2	0.3	0.5
Brass	Smooth	12 hr	-	-	-	0.1	-	0.1	0.2	0.3
		24 hr	-	0.1	0.1	0.3	0.1	-	0.2	0.3
		36 hr	-	0.1	0.2	0.3	0.1	0.1	0.2	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.2	0.3
		24 hr	-	-	-	0.2	0.1	0.2	0.2	0.3
		36 hr	-	-	0.2	0.3	0.1	0.2	0.3	0.6
Silver	Smooth	12 hr	-	-	-	0.1	-	0.1	0.1	-
		24 hr	-	-	0.3	0.5	-	-	-	-
		36 hr	-	0.1	0.4	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.1	0.1	0.1	0.2	0.1
		24 hr	-	-	0.2	0.6	0.1	0.2	0.2	-
		36 hr	-	0.1	0.2	0.6	0.1	0.2	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/135 ppm PH_3/3.2% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.4	1.0	-	0.1	0.4	0.9
		24 hr	2.4*	3.3*	1.2	1.1	0.8	1.0	1.0	1.0
		36 hr	21.2*	16.0*	2.9	2.8	4.2	6.4	1.8	1.8
	Rough	12 hr	0.3*	0.4*	0.6	0.9	0.3	0.4	0.5	0.7
		24 hr	3.9*	3.5*	2.4	2.1	1.2	1.7	1.6	0.5
		36 hr	27.3*	16.2*	4.9	3.4	4.0	7.7	3.6	2.8
Brass	Smooth	12 hr	0.1	-	0.7	0.5	-	0.2	0.6	0.6
		24 hr	-	-	1.6	0.9	0.4	0.6	1.2	0.7
		36 hr	0.1	0.3	3.0	2.0	1.0	0.5	2.0	1.8
	Rough	12 hr	-	-	0.5	0.4	-	0.3	0.5	0.4
		24 hr	0.1	0.1	0.5	0.5	0.3	0.7	0.9	0.8
		36 hr	0.1	-	1.6	1.7	1.4	1.1	1.6	1.8
Silver	Smooth	12 hr	-	0.1	0.1	0.3	-	-	-	-
		24 hr	-	-	0.1	0.2	-	-	-	0.1
		36 hr	0.1	-	0.9	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.3	0.1	0.2	0.1	0.1
		24 hr	-	0.1	0.2	0.6	0.1	0.1	0.1	0.1
		36 hr	0.1	0.1	0.7	1.0	-	0.1	-	-

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	0.3	0.8	1.2	-	0.2	0.4	0.7
		24 hr	2.9*	3.4*	2.3	3.3	1.3	1.0	0.9	1.8
		36 hr	23.3*	13.8*	5.1	4.5	4.8	4.2	4.6	3.6
	Rough	12 hr	0.1*	0.7*	1.1	1.1	0.2	0.4	0.8	0.9
		24 hr	5.6*	4.5*	3.3	2.4	1.9	1.6	2.1	1.6
		36 hr	26.0*	13.3*	6.1	3.9	5.2	4.5	4.2	2.6
Brass	Smooth	12 hr	-	0.1	0.9	1.1	0.1	0.2	0.6	0.9
		24 hr	-	0.1	0.8	1.2	0.1	0.7	0.8	1.6
		36 hr	-	0.9	1.5	1.6	0.1	3.1	1.6	1.6
	Rough	12 hr	-	0.1	0.4	0.9	0.2	0.2	0.6	0.9
		24 hr	-	-	0.4	0.9	0.1	0.7	1.4	1.5
		36 hr	-	0.3	0.8	1.9	0.2	1.6	1.2	2.2
Silver	Smooth	12 hr	-	-	0.1	0.4	-	-	-	-
		24 hr	-	-	0.5	0.6	-	-	-	-
		36 hr	0.1	0.1	0.4	1.4	-	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.1
		24 hr	-	0.1	0.1	0.7	0.1	-	0.1	-
		36 hr	0.1	0.1	0.7	1.2	0.1	-	0.1	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/220 ppm PH_3/3.2%CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	1.2*	1.2	0.9	0.1	0.5	1.0	0.7
		24 hr	2.9*	8.2*	2.8	1.9	0.7	3.6	2.8	1.6
		36 hr	31.6*	23.4*	7.8	5.3	4.2	5.6	6.0	4.3
	Rough	12 hr	1.2*	1.8*	1.8	1.3	0.3	0.8	1.1	1.0
		24 hr	2.0*	8.6*	7.8	3.7	0.6	2.4	5.0	2.7
		36 hr	21.9*	13.8*	8.9	6.3	3.7	4.4	6.7	4.8
Brass	Smooth	12 hr	0.1	-	3.1	0.9	0.1	0.4	3.1	0.9
		24 hr	0.1	-	6.5	2.7	0.2	0.6	6.5	2.3
		36 hr	0.2	0.9	20.4	9.3	1.8	2.1	10.7	5.9
	Rough	12 hr	0.1	-	1.5	1.0	0.2	0.5	1.4	1.2
		24 hr	-	-	0.9	2.3	0.5	0.7	1.5	2.4
		36 hr	-	0.1	7.4	4.4	1.7	1.7	5.1	3.9
Silver	Smooth	12 hr	0.1	-	0.1	0.1	-	0.1	-	-
		24 hr	0.1	0.1	0.1	0.7	0.1	-	-	-
		36 hr	-	0.1	0.6	1.3	0.1	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	0.2	0.1	0.2	0.1
		24 hr	-	-	0.2	0.9	0.1	0.2	-	0.1
		36 hr	-	0.3	0.4	1.3	0.2	0.2	0.1	-

The solder samples gained no weight under these test conditions
*Samples were wet
25 & 50% RH - samples mounted parallel
15 & 75% RH - samples mounted radially

30C/220 ppm PH_3/4.5% CO_2

Sample Area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	1.6	1.3	0.9	1.9	0.8	1.1	0.5	1.4
		24 hr	27.9*	9.0*	2.3	6.0	6.8	4.2	2.2	4.9
		36 hr	21.2*	13.5*	5.0	11.1	4.8	4.7	3.6	8.9
	Rough	12 hr	6.9*	8.2*	1.4	2.0	3.4	3.7	1.0	1.6
		24 hr	18.3*	6.8*	5.0	9.3	4.1	4.1	3.1	5.9
		36 hr	31.9*	34.0*	9.9	12.6	6.1	7.4	5.9	8.1
Brass	Smooth	12 hr	-	0.2	3.8	1.0	-	0.6	1.4	1.2
		24 hr	-	-	7.4	6.9	-	-	2.9	4.8
		36 hr	-	0.3	14.7	5.5	1.0	3.8	6.6	4.3
	Rough	12 hr	-	-	0.8	1.1	0.4	0.2	0.7	1.6
		24 hr	-	-	1.5	1.4	0.5	0.2	1.3	3.4
		36 hr	-	-	1.9	0.9	1.2	0.2	2.8	3.2
Silver	Smooth	12 hr	-	-	0.4	0.1	-	0.2	-	-
		24 hr	-	-	0.3	0.2	-	-	-	0.1
		36 hr	-	0.1	0.4	0.8	-	-	0.1	0.1
	Rough	12 hr	-	-	0.2	0.3	-	0.5	0.3	0.1
		24 hr	-	-	0.3	0.3	-	-	-	0.1
		36 hr	-	0.1	0.3	0.6	-	0.1	0.1	0.2

The solder samples gained no weight under these test conditions
* Samples were wet
All samples mounted radially

40C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.1	0.2	-	0.1	0.1	0.1
		24 hr	0.2	-	0.5	0.3	0.1	-	0.4	0.1
		36 hr	0.3	0.1	0.7	0.4	0.2	-	0.5	0.3
	Rough	12 hr	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
		24 hr	0.4*?	0.1	0.4	0.3	0.2	0.1	0.5	0.2
		36 hr	2.4*	0.3	1.1	0.4	1.0	0.3	0.8	0.4
Brass	Smooth	12 hr	-	-	0.1	0.2	0.1	-	0.1	0.3
		24 hr	-	-	0.3	0.4	0.1	-	0.3	0.2
		36 hr	0.1	0.2	0.3	0.5	0.2	-	0.4	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.3	0.2
		24 hr	-	-	0.1	0.2	0.2	-	0.5	0.4
		36 hr	-	-	0.1	0.3	0.3	0.1	0.5	0.6
Silver	Smooth	12 hr	-	-	0.2	0.2	-	-	-	-
		24 hr	-	-	0.6	0.6*	-	-	-	-
		36 hr		-	0.2	1.3*	-	-	-	-
	Rough	12 hr	0.1	-	0.4	0.6	-	0.1	0.2	0.1
		24 hr	-	0.2	0.7	1.3	0.2	0.1	0.2	0.1
		36 hr	0.2	0.3	1.1	1.6	0.1	0.1	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

40C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25%+ RH	50% RH	75% RH	15% RH	25%+ RH	50% RH	75% RH
Copper	Smooth	12 hr	-	1.0	1.6	1.2	0.1	0.7	1.2	1.0
		24 hr	8.4*	4.5	3.8	2.4	2.1	1.7	2.7	2.3
		36 hr	40.9*	19.1	5.9	5.0	5.9	7.9	3.2	4.1
	Rough	12 hr	1.7*	3.7	2.3	1.2	0.6	1.7	1.9	1.0
		24 hr	22.6*	13.8	5.3	2.2	3.7	9.0	3.6	1.9
		36 hr	45.2*	24.5	8.6	4.1	6.0	13.8	5.5	3.6
Brass	Smooth	12 hr	-	0.3	0.6	0.7	0.2	0.6	0.7	0.9
		24 hr	0.1	1.7	1.5	2.2	0.4	1.6	2.3	2.3
		36 hr	0.7	11.9*	3.2	4.7	0.4	6.1	3.7	3.8
	Rough	12 hr	-	-	0.2	0.8	0.4	0.9	0.8	0.9
		24 hr	-	-	0.4	1.6	0.2	1.5	1.1	1.7
		36 hr	-	2.1	1.2	5.6	0.4	3.9	2.3	4.4
Silver	Smooth	12 hr	-	-	0.3	0.7*	-	-	-	-
		24 hr	0.4	0.1	0.4	1.3*	-	-	-	0.1
		36 hr	-	0.3	1.3	2.0*	-	-	-	-
	Rough	12 hr	-	0.1	0.6	1.0	0.4	0.3	0.2	0.2
		24 hr	0.1	0.1	1.1	1.3	0.3	0.4	0.2	0.2
		36 hr	0.1	0.3	2.0	1.5	0.2	0.2	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel
+A power failure near the end of the experiment turned off the PH^3 and caused the humidity to rise.
The copper samples had obviously been wet during the experiment but were dry when removed.

40C/220 ppm PH_3/3.5% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.2*	7.4*	4.5	3.5	2.0	2.9	3.6	2.4
		24 hr	19.8*	29.3*	10.5	7.4	6.2	10.2	7.6	5.4
		36 hr	37.7*	64.0*	17.6	11.9	10.6	18.7	12.3	11.1
	Rough	12 hr	9.0*	12.9*	5.7	4.0	2.2	5.3	4.4	3.2
		24 hr	22.8*	36.6*	15.7	9.9	4.7	11.0	9.3	6.0
		36 hr	34.6*	62.4*	19.8	18.8	11.9	16.4	12.0	12.2
Brass	Smooth	12 hr	0.1	0.2	1.5	3.2	1.1	0.9	1.1	2.4
		24 hr	0.2	2.2	4.2	2.8	2.9	5.7	5.0	4.4
		36 hr	1.2*?	25.6*	9.9	6.7	0.3	12.1	9.8	7.3
	Rough	12 hr	0.1	0.1	0.2	1.3	0.9	1.7	1.2	2.2
		24 hr	-	-	2.3	2.0	1.8	3.8	3.5	3.5
		36 hr	-	2.1	5.4	7.7	0.2	1.6	6.0	6.0
Silver	Smooth	12 hr	0.1	-	0.4*	0.8*	-	-	-	-
		24 hr	0.1	-	0.8*	1.2*	-	0.1	-	-
		36 hr	0.2	0.3	1.1*	1.6*	-	-	-	-
	Rough	12 hr	0.1	0.1	0.3	0.8	0.2	0.4	0.2	0.3
		24 hr	0.1	-	0.5	1.3	0.2	0.3	0.2	0.2
		36 hr	0.1	0.2	1.0	2.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

40C/220 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.5*	6.0*	4.0	4.2	2.1	2.6	3.6	4.4
		24 hr	20.1*	33.7*	8.9	8.5	6.1	8.6	8.0	7.3
		36 hr	34.6*	55.7*	13.4	16.9	9.4	15.1	11.8	11.6
	Rough	12 hr	8.2*	11.2*	5.9	3.5	2.6	5.1	5.1	2.9
		24 hr	21.9*	40.3*	12.7	8.7	6.1	13.1	9.3	8.1
		36 hr	33.4*	52.6*	18.3	14.6	9.5	15.4	13.1	11.8
Brass	Smooth	12 hr	0.1	0.4	2.4	3.5	1.3	0.6	2.1	3.0
		24 hr	-	14.3*	14.8	10.1	1.7	7.4	10.2	8.2
		36 hr	11.1*	31.2*	32.4	16.7	6.4	11.5	16.9	11.5
	Rough	12 hr	-	0.1	0.5	2.0	0.3	1.2	1.4	2.5
		24 hr	-	1.8	2.8	4.6	1.9	4.4	3.3	4.3
		36 hr	0.1	16.9*	14.8	6.5	1.9	7.4	10.5	7.8
Silver	Smooth	12 hr	-	0.2	0.7*	1.4	-	0.1	-	-
		24 hr	0.2	1.1*	1.1*	1.5*	-	0.1	-	-
		36 hr	-	1.4*	2.2*	2.7*	-	-	-	-
	Rough	12 hr	-	0.2	0.9	1.3	0.5	0.4	0.2	0.3
		24 hr	0.1	0.2	1.4	1.8	0.5	0.5	0.2	0.1
		36 hr	0.3	0.9	2.3	2.5	0.3	0.2	0.3	-

The solder samples gained no weight under these test conditions

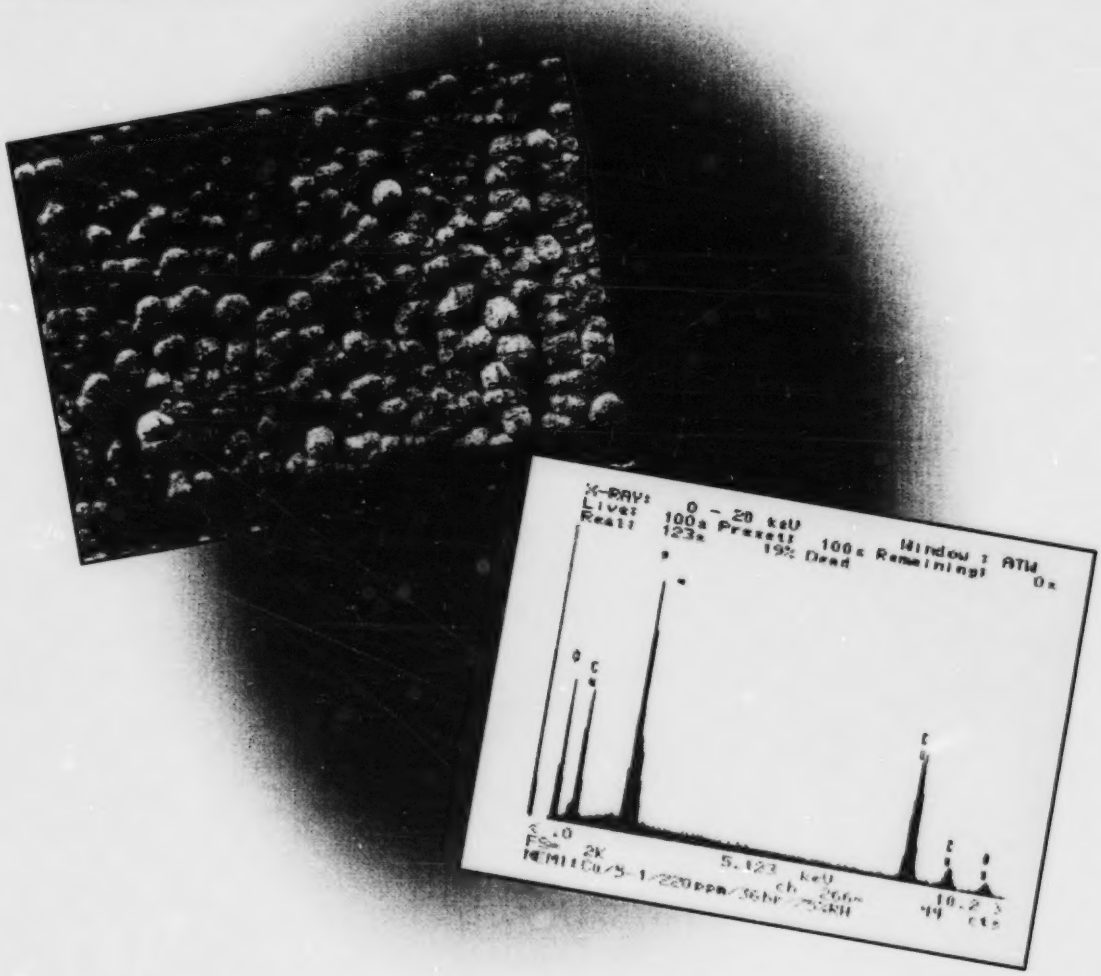
*Samples were wet

All samples mounted parallel

Effets corrosifs de la phosphine, du dioxyde de carbone, de la chaleur et de l'humidité sur le matériel électronique

Canada

Le rôle prépondérant du Canada dans le développement de produits de substitution du bromure de méthyle



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Effets corrosifs de la phosphine, du dioxyde de carbone, de la chaleur et de l'humidité sur le matériel électronique

Le rôle prépondérant du Canada dans le développement de produits de substitution du bromure de méthyle

Août 1998

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En collaboration avec :
le groupe de travail industrie/gouvernement sur le bromure de méthyle;
Environnement Canada; le Department of Agriculture des États-Unis;
et la Canadian National Millers Association

Remerciements

La présente étude a été parrainée par le Department of Agriculture des États-Unis, Agriculture et Agroalimentaire Canada, Environnement Canada, Ressources naturelles Canada et la Canadian National Millers Association, avec l'appui de l'industrie canadienne de transformation des aliments, de l'Association canadienne de la lutte contre les parasites et de David Mueller de Fumigation Service and Supply Inc., Indianapolis (IN, É.-U). Ce projet a été réalisé sous les auspices du groupe de travail Canada/É.-U. sur les produits de substitution du bromure de méthyle.

Graphisme et impression :
Bonanza Printing & Copying Centre Inc., Ottawa (ON)

Imprimé au Canada, sur du papier recyclé

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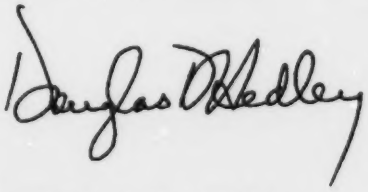
Avant-propos

Le Protocole de Montréal sur les substances appauvrissant la couche d'ozone est un accord mondial, dont le but est de protéger la couche d'ozone en réduisant la production de ces substances. Les pays développés signataires du Protocole de Montréal - dont font partie le Canada et les États-Unis - doivent avoir complètement cessé de produire et de consommer du bromure de méthyle, d'ici 2005.

Il est devenu essentiel de remplacer le bromure de méthyle utilisé comme fumigant des sols, des marchandises et des bâtiments depuis qu'il fait l'objet de limitations en tant que substance appauvrissant la couche d'ozone. Des progrès sont réalisés grâce à des programmes gouvernementaux de recherche et à la mise au point de technologies et de produits de substitution dans l'industrie. Toutefois, il reste beaucoup à faire pour combattre efficacement les nuisibles et les maladies des plantes en agriculture et lors de la transformation des aliments.

Afin d'accroître le plus possible la collaboration des chercheurs et d'accélérer la mise au point de solutions de remplacement, Agriculture et Agroalimentaire Canada (AAC) et le Department of Agriculture des États-Unis (USDA) ont créé un groupe de travail informel sur les produits de substitution du bromure de méthyle. Une entente a été conclue afin d'aider les chercheurs scientifiques et l'industrie à travailler ensemble sur des problèmes et des projets communs et à partager les résultats de ces recherches. Puisque des quantités importantes de bromure de méthyle sont utilisées au Canada pour la fumigation des locaux où se déroulent des opérations de meunerie ou de transformation des aliments, et à un degré moindre aux États-Unis, on a proposé au Canada de jouer au sein du groupe de travail, le rôle directeur dans ce domaine. Le présent rapport est le deuxième issu de la collaboration, financée conjointement, entre des chercheurs d'AAC, du service de recherche agricole de l'USDA et l'industrie privée, pour mettre au point des produits de substitution du bromure de méthyle.

Cette étude de laboratoire est aussi représentative d'un élément clé du succès du développement de l'agroalimentaire. Les partenariats de recherche avec l'industrie et d'autres organismes gouvernementaux sont une des pierres angulaires des programmes d'AAC et de l'USDA. À cet égard, le travail sur la corrosion due à la phosphine n'aurait pas pu être réalisé sans l'expertise de Robert Brigham (Ph.D.) du Centre canadien de la technologie des minéraux et de l'énergie (CANMET). De plus, nous avons apprécié les conseils dispensés par l'industrie, en particulier nous voudrions remercier David Mueller (Fumigation Service & Supply Inc.) pour sa perspicacité et pour nous avoir fourni des échantillons corrodés provenant de fumigation sur le terrain. Les résultats de cette étude en laboratoire peuvent être facilement appliqués sur le terrain et serviront à assurer une lutte efficace contre les nuisibles et à réduire le risque de corrosion de l'équipement électrique par la phosphine. Nous voudrions remercier les personnes y ayant collaboré pour leurs efforts.



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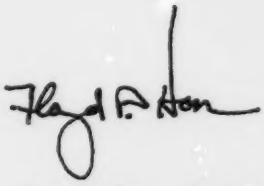

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Résumé

On a exposé quatre métaux - l'argent (contacts électriques), le cuivre (conducteurs électriques), le laiton (composants électriques) et de la soudure - aux conditions expérimentales suivantes, soigneusement contrôlées et à l'état stationnaire, simulant des paramètres utilisés lors de fumigation :

- trois températures : 20, 30 et 40 °C
- trois concentrations de phosphine : 35, 135 et 220 ppm
- quatre niveaux d'humidité relative : 15, 25, 50 et 75 %
- deux niveaux de CO_2 : 3,5 et 5 %
- trois durées d'exposition : 12, 24 et 36 heures

Au cours des expositions, le phosphore de la phosphine a été oxydé en présence de vapeur d'eau pour produire des dépôts superficiels d'oxydes de phosphore et les métaux se sont oxydés (corrodés) dans l'air à une vitesse limitée par la disponibilité de l'oxygène, entraînant un gain de poids. On a éliminé les produits de corrosion résultant de l'oxydation des métaux (et les oxydes de phosphore) en immergeant le métal dans une solution 50/50 de HCl, jusqu'à faire apparaître le métal nu. La perte de poids a permis de calculer la vitesse de corrosion du métal.

On a jugé que les effets de la rugosité de la surface et de la concentration de dioxyde de carbone étaient minimes et ces données cinétiques ont donc été regroupées lorsque l'on a représenté les effets moyens des autres variables - humidité relative, température, concentration de phosphine et durée d'exposition.

On a utilisé un microscope à balayage électronique (SEM) avec un dispositif d'analyse aux rayons X à dispersion d'énergie (EDAX) pour observer la morphologie et déterminer la chimie des dépôts superficiels sur les éprouvettes métalliques exposées lors de ces expériences. On a aussi utilisé le SEM pour mettre en évidence la morphologie de la corrosion de larges bandes de cuivre exposées à la fumigation sur le terrain. La morphologie typique de la corrosion du cuivre comprend des zones non attaquées, des zones d'attaque généralisée et des zones comportant des piqûres. Le laiton présentait une morphologie similaire, alors que l'argent et la soudure n'étaient pas attaqués.

Au cours de cette étude, on a obtenu un résultat inattendu lors de la caractérisation des régimes sec et humide du cuivre exposé à de la phosphine, en fonction de l'humidité relative. Le cuivre ne produit un dépôt superficiel noir, brillant, humide, qu'aux faibles taux d'humidité relative (25 % ou moins); cette observation est contre-intuitive et contraire aux quelques cas rapportés. On a observé des dépôts superficiels cristallins secs sur le cuivre, uniquement aux taux élevés d'humidité relative (50 % ou plus).

Le tableau ci-dessous résume les observations faites au cours de l'étude, sur des échantillons métalliques de différentes origines.

MÉTAL	SOURCE	GAIN DE POIDS	CORROSION
Cuivre	La présente étude Échantillons fournis par Mueller	Considérable	Considérable
Nickel	Calculatrice de Mueller Appareil photo de Mueller	Oui	?
Laiton	La présente étude	Oui	Oui
Argent	La présente étude Fumigation effectuée par Mueller	Oui	Non
Acier inoxydable	Appareil photo de Mueller	Aucune signature P	Aucune trace
Soudure	La présente étude Calculatrice de Mueller Fumigation effectuée par Mueller	Non	Non

On doit noter que les dépôts superficiels et la morphologie de la corrosion étaient identiques, qu'ils soient produits en laboratoire ou lors de fumigation sur le terrain.

On a trouvé trois mécanismes possibles de défaillance du matériel électronique exposé à de la phosphine :

- résistance importante des contacts due à l'accumulation de dépôts superficiels non conducteurs
- court-circuit électrique dû à la formation de phases liquides conductrices
- rupture des circuits due à la corrosion des métaux

Légende de schéma

Figure 1a. Micrographie électronique à balayage (mode BSE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 12 heures, à 30 °C et à une HR de 75 %.

Figure 1b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 12 heures, à 30 °C et à une HR de 75 %.

Figure 2a. Micrographie électronique à balayage (mode BSE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 24 heures, à 30 °C et à une HR de 75 %.

Figure 2b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 24 heures, à 30 °C et à une HR de 75 %.

Figure 3a. Micrographie électronique à balayage (mode BSE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 36 heures, à 30 °C et à une HR de 75 %.

Figure 3b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 36 heures, à 30 °C et à une HR de 75 %.

Figure 4. Micrographie électronique à balayage (mode SE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 36 heures, à 30 °C et à une HR de 75 %.

Figure 5. Spectre EDAX des dépôts superficiels de la figure 4.

Figure 6a. Micrographie électronique à balayage (mode SE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 12 heures, à 40 °C et à une HR de 15 %.

Figure 6b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 12 heures, à 40 °C et à une HR de 15 %.

Figure 7a. Micrographie électronique à balayage (mode SE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 24 heures, à 40 °C et à une HR de 15 %.

Figure 7b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 24 heures, à 40 °C et à une HR de 15 %.

Figure 8a. Micrographie électronique à balayage (mode SE) de dépôts superficiels sur du cuivre exposé à 220 ppm de PH_3 pendant 36 heures, à 40 °C et à une HR de 15 %.

Figure 8b. Micrographie électronique à balayage (mode SE) de cuivre nettoyé chimiquement après une exposition à 220 ppm de PH_3 pendant 36 heures, à 40 °C et à une HR de 15 %.

Figure 9. Spectre EDAX des grands dépôts superficiels noirs de la figure 8a.

Figure 10. Micrographie électronique à balayage (mode BSE) de dépôts superficiels sur de l'argent exposé à 220 ppm de PH_3 pendant 12 heures, à 40 °C et à une HR de 15 %.

Figure 11. Micrographie électronique à balayage (mode BSE) de dépôts superficiels sur de l'argent exposé à 220 ppm de PH_3 pendant 12 heures, à 40 °C et à une HR de 75 %.

Figure 12. Effet de l'humidité relative sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 13. Effet de l'humidité relative sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 14. Effet de l'humidité relative sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) de l'argent.

Figure 15. Effet de la température sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 16. Effet de la température sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 17. Effet de la température sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) de l'argent.

Figure 18. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 19. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 20. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 21. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 22. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 23. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) de l'argent.

Figure 24. Effet de la concentration de phosphine sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) de l'argent.

Figure 25. Effet de la durée d'exposition sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 26. Effet de la durée d'exposition sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du cuivre.

Figure 27. Micrographie électronique à balayage (mode BSE) montrant l'étendue de la couverture de la surface de l'échantillon de cuivre de la figure 6a (mode SE).

Figure 28. Effet de la durée d'exposition sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 29. Effet de la durée d'exposition sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) du laiton.

Figure 30. Effet de la durée d'exposition sur le gain de poids (dû au dépôt d'oxydes de phosphore) et sur la perte de poids (due à la corrosion) de l'argent.

EFFETS CORROSIFS DE LA PHOSPHINE, DU DIOXYDE DE CARBONE, DE LA CHALEUR ET DE L'HUMIDITÉ SUR LE MATÉRIEL ÉLECTRONIQUE

Introduction

Le problème de la corrosion des métaux par la phosphine a été étudié lors de travaux antérieurs au Canada (1) et lors d'études plus récentes au Danemark (2) et aux États-Unis (3,4). Toutefois, les conditions d'exposition qui favorisent une attaque et le processus de corrosion ne sont toujours pas très bien compris. La présente étude visait à quantifier, dans des conditions de laboratoire soigneusement contrôlées, la cinétique de la corrosion et la morphologie des métaux communément utilisés dans le matériel électronique.

On a choisi d'étudier quatre métaux - l'argent (contacts électriques), le cuivre (conducteurs électriques), le laiton (composants électriques) et la soudure. On a testé des matériaux présentant des surfaces lisses ou des surfaces abrasées afin d'accroître la probabilité d'adsorption de l'eau à un taux d'humidité relative donné - condition équivalant à la présence de poussière sur la surface. On pense que le comportement à la corrosion de ces quatre matériaux permettra de déterminer les endroits les plus sensibles aux problèmes de corrosion des composants électriques.

Les paramètres testés étaient les suivants :

- trois températures : 20, 30 et 40 °C
- trois concentrations de phosphine : 35, 135 et 220 ppm
- quatre taux d'humidité relative : 15, 25, 50 et 75 %
- deux niveaux de CO_2 : 3,5 et 5 %
- trois durées d'exposition : 12, 24 et 36 heures

Expérimentation

L'appareillage expérimental a été conçu de manière à faciliter la variation indépendante de toutes les variables. À cette fin, un courant d'air (1 litre/minute) a été saturé d'eau à basse température dans un bain à température constante Haake, modèle K (pour donner une humidité relative de 100 %), puis la température de ce courant d'air a été portée, dans un second bain Haake, à la température d'essai (20, 30 ou 40 °C), de manière à réduire l'humidité relative à un niveau prédéterminé. De plus, du CO_2 (provenant d'une bouteille de gaz comprimé pur) et de la PH_3 (provenant d'un mélange de gaz, N_2 - 0,5 % de PH_3, acheté auprès de Matheson) ont été introduits dans ce courant d'air au niveau du second bain, afin d'y être préchauffés et mélangés. Cette dilution faisait baisser l'humidité relative du courant porteur qui était ajustée par tâtonnement au niveau désiré, à l'aide d'un hygromètre VWR. Les débits de gaz ont été réglés à l'aide de débitmètres massiques et la concentration de PH_3 a été vérifiée périodiquement, tout au long des expériences de 36 heures, à l'aide d'un indicateur de PH_3 PortaSens. Les débits de CO_2, d'air et de N_2 ont été mesurés au début et à la fin de chaque expérience, à l'aide de débitmètres à bulle de

savon. On a ainsi constaté que la stabilité à long terme des débits se situait à ±2 % près de la valeur indiquée par le fabricant des débitmètres massiques.

On a débuté chaque expérience en plaçant 8 échantillons métalliques pesés, mesurant approximativement 50 x 13 x 0,1 mm (surface de 0,13 dm^2), dans des gobelets en polyéthylène dont les côtés et le dessus avaient été partiellement enlevés, afin que les gaz puissent y entrer et sortir librement. Dans les premières expériences réalisées, les échantillons ont été montés radialement dans les gobelets, mais dans les expériences suivantes, ils ont été montés en parallèle, ce qui a semblé améliorer la reproductibilité des résultats. On a exposé du cuivre (99,9 %), du laiton (cales minces de laiton jaune 70/30), de l'argent (99,9 %) et de la soudure (Pb-Sn 50/50) ayant soit une surface laminée, soit une surface soumise à une abrasion à l'aide de SiC de granulométrie 120. Avant l'exposition, les échantillons ont été nettoyés chimiquement à l'aide d'une solution 50/50 de HCl pendant 2 minutes. On a placé les gobelets contenant les échantillons dans 3 chambres et on a fait circuler le gaz de manière à obtenir des expositions de 12, 24 et 36 heures. On a d'abord établi des conditions stationnaires de température et d'humidité relative, indiquées par un hygromètre numérique, à l'aide d'un mélange d'air, de CO_2 et de N_2. Une fois le système stabilisé, on a retiré l'hygromètre et on a tourné le robinet à deux voies de manière à remplacer le courant de N_2 par le mélange N_2 - 0,5 % PH_3. On a ensuite surveillé régulièrement que la température des bains et la concentration de PH_3 restaient stables.

Après chaque passage, les échantillons ont été à nouveau pesés, dans l'état où ils étaient retirés de la chambre, nettoyés jusqu'au métal nu par immersion pendant 2 minutes dans une solution de HCl 50/50, puis pesés de nouveau.

Résultats

a. Cinétique

Au cours de l'exposition, le phosphore contenu dans la phosphine peut s'oxyder à la surface du métal, en présence de vapeur d'eau, et passer d'un état de valence -3 à un état d'oxydation plus élevé, selon les réactions suivantes (5) :

- oxydation de P de l'état -3 à l'état +1 (catalysée par Cu, Ni, Pd, C)
  $PH_3 + 2H_2O = H_3PO_2 + 4H^+ + 4e^-$ (acide orthophosphoreux)
- oxydation de P de l'état -3 à l'état +3
  $PH_3 + 3H_2O = H_3PO_3 + 6H^+ + 6e^-$ (acide phosphoreux)
- oxydation de P de l'état -3 à l'état +5
  $PH_3 + 4H_2O = H_3PO_4 + 8H^+ + 8e^-$ (acide phosphorique)

Ces réactions produisent des dépôts superficiels d'oxydes de phosphore et il en résulte un gain de poids. Dans les tableaux de l'appendice A, ces gains de poids sont donnés pour le cuivre, le laiton et l'argent, mais pas pour la soudure qui n'en présentait aucun, quelles que soient les conditions d'exposition.

Ces tableaux de données indiquent aussi que certains échantillons étaient humides et d'autres secs lorsqu'on les retirait de la chambre. On résume ces observations ci-dessous :

Métal	Température	H.R. de 15 et 25%	H.R. de 50 et 75%
Cuivre	Toutes	Humide	Sec
Laiton	40 °C	Humide	Sec
	20 et 30 °C	Sec	Sec
Argent	Toutes	Sec	Humide
Soudure	Toutes	Sec	Sec

Le comportement du cuivre, c'est-à-dire humide lorsque l'humidité relative est faible et sec lorsqu'elle est élevée, est inattendu et contre-intuitif. Par contre, le comportement de l'argent est plus proche du comportement attendu. Cependant, comme le montre le changement de poids, le mouillage était minime. Les échantillons d'argent humides apparaissaient troubles à l'oeil nu et sous un microscope stéréo à faible grossissement, de petites « gouttes de rosée » étaient visibles à la surface. Le comportement du laiton était intermédiaire entre ceux du cuivre et de l'argent, le mouillage du cuivre en présence d'un faible taux d'humidité relative, n'étant observé qu'à 40 °C . Dans aucune des conditions expérimentales utilisées, on n'a pu mesurer de gain de poids dans le cas de la soudure et aucune trace de P n'a été mise en évidence par analyse par rayons X à dispersion d'énergie (EDAX).

Le cuivre, le laiton et l'argent sont thermodynamiquement stables dans des solutions acides non oxydantes et ne se corrodent donc pas dans ces solutions. Toutefois, ils s'oxydent (se corrodent) à l'air, à une vitesse limitée par la disponibilité de l oxygène, et toute tendance à la passivation est empêchée dans une solution à faible pH. Les produits de corrosion de l'oxydation des métaux (et les oxydes de phosphore déposés lors des réactions susmentionnées) peuvent être éliminés, jusqu'à faire apparaître le métal nu, par immersion dans une solution 50/50 de HCl, un acide non oxydant. On peut ensuite déduire la vitesse de corrosion du métal d'après la perte de poids mesurée. Dans l'appendice A, on donne aussi les pertes de poids mesurées après décapage jusqu'au métal nu.

b. Morphologie

On a utilisé un microscope à balayage électronique (SEM) avec EDAX pour observer la morphologie des dépôts superficiels des éprouvettes métalliques exposées lors de ces expériences et

The wet and dry morphologies observed on brass were similar to those discussed above for copper but in the case of silver, the extent of surface coverage was minimal. Figure 10 shows the very limited extent of coverage on silver exposed for 12 hours at 40°C to 220 ppm PH_3 (dry regime for silver) and Figure 11 shows the increased, but still small, coverage at 75% RH (wet regime). No corrosion was found on chemically cleaned silver coupons.

In addition to laboratory coupons, the following observations have been made with respect to copper samples exposed in field fumigations(3,4)

- surface deposits on the copper are mainly colourless to slightly bluish crystals. A few random dark circular deposits seem to be associated with surface dust.
- these deposits are not electrical conductors and charge in the electron beam of the SEM.
- EDAX shows that the elements present are Cu, P and O.
- surface deposits nucleate at surface imperfections such as rolling marks and grow rapidly to increase surface coverage but in a non-linear way
- when the surface deposits were removed in 50/50 HCl, the copper substrate showed areas of no attack, areas of general attack and other areas with pitting.

Discussion

Because single coupons of each metal were exposed under each of the steady-state exposure conditions, the weight change data in Appendix A are characterized by considerable scatter and are not amenable to statistical analysis. However, a number of interesting trends are discussed below.

Effect of Surface Roughness

In Appendix A, any differences in weight change between smooth samples and samples abraded with 120 grit SiC paper seemed to be minimal and within the sample to sample scatter in the data. Consequently, the data for smooth and rough samples were averaged for trend analysis.

Effect of Carbon Dioxide Concentration

Differences in CO_2 concentrations (3.2% vs. 4.5% and 3.5% vs. 5.0%) had minimal effect on weight change data and results at high and low CO_2 were averaged for trend analysis. If CO_2 has an effect, it may be a small one in defining equilibrium conditions for wet/dry morphology - see for example the behaviour of brass in 220 ppm PH_3 at 40°C and 25% RH in 3.5 vs. 5% CO_2 (Appendix A).

Effect of Relative Humidity

Copper is clearly a special case where the effect of relative humidity on weight gain is entirely counter-intuitive. At 15 and 25% relative humidity, copper coupons were observed to be wet after exposure whereas at the higher humidity levels investigated - 50 and 75% RH - the copper samples were invariably dry and coated with crystalline material. In Figure 12, the average weight change

of smooth and rough copper coupons exposed to 3.5 and 5% CO_2 and 220 ppm PH_3 for 36 hours is plotted as a function of RH for the 3 exposure temperatures. The effect of wetness on weight gain is apparent at 40 and 30°C but not at 20°C. Wetness had only a minimal effect on weight loss (corrosion) as might be expected in the case were corrosion rate is controlled by oxygen availability.

For brass weight change results averaged in the same way and shown in Figure 13, it should be noted that wetness was observed only at lower relative humidities and only at 40°C. This was the case at lower PH_3 concentrations as well. As with the copper, weight loss (corrosion) was relatively unaffected by wetness and the corrosion rates of copper and brass were similar under most conditions as would be expected where oxygen availability controlled. Weight gains, however, were consistently lower on brass than on copper.

As shown in Figure 14, the data for silver (averaged in the same way as for copper and brass above) reflects the intuitive relationship of increasing weight change with increasing RH and, indeed, small droplets of moisture were observed at higher relative humidities. Based on the minute weight losses and morphological observations, it can be concluded that silver does not corrode in phosphine.

Effect of Temperature

An example of the effect of temperature on reaction kinetics is shown in Figure 15 for copper. In the wet regime (15 and 25% RH), increasing temperature has a significant effect on both weight gain and weight loss kinetics. In the dry regime (50 and 75% RH), only the highest temperature (40°C) leads to significant increases in reaction rates.

Unlike copper, brass (shown in Figure 16) is dry at low relative humidities (15 and 25%) and low temperatures (20 and 30°C) and shows no temperature dependence in this range. With the onset of the wet regime at 40°C, kinetics increase dramatically at 25% RH but are much more muted at 15%.

The weight gain kinetics of silver shown in Figure 17 are greatly accelerated with increasing temperature at all relative humidity levels but the absolute values are very small relative to copper and brass under the same conditions. Silver does not corrode in the temperature range 20 to 40°C.

Effect of Phosphine Concentration

In general, weight changes of copper, brass and silver vary in a linear way with increasing PH_3 concentrations. For example, Figures 18, 19 and 20 show the weight gains and weight losses on copper at 20, 30 and 40°C, respectively, with changes in PH_3 concentration from 35 to 220 ppm. At 35 ppm PH_3, the weight changes are essentially zero (<0.7mg in 36 hours) at all temperatures but change dramatically as PH_3 increases to 220 ppm. In the dry regime (50 and 75% RH), the weight increase appears to be linear while in the wet regime (15 and 25% RH) the increase is somewhat erratic but the trend is clearly upward and strongly temperature dependent. Weight losses

(corrosion) of copper also increase with PH_3 concentration but are insensitive to wet/dry variations except at the lowest temperature. The behaviour of brass parallels that of copper as shown in Figures 21 and 22 at 30 and 40°C, respectively, but with smaller overall weight changes.

Silver at 30°C (Figure 23) experiences minimal weight increases (<1mg in 36 hours) and is relatively insensitive to PH_3 concentration but at 40°C (Figure 24) the weight gain trends are similar to copper and brass. The corrosion rate of silver can be taken as zero at all PH_3 concentrations and temperatures.

Effect of Exposure Time

Reaction kinetics of metals in PH_3 as measured by weight change has been observed to be linear with time or to accelerate with time. Accelerating weight increase is consistent with nucleation at points on the surface, grow of these deposits with time leading to complete surface coverage and subsequent linear kinetics. This kind of behaviour is evident in Figures 1a, 2a and 3a for copper at 30°C. The related kinetics in Figure 25 show the weight change accelerating with time. However, at 40°C, Figure 26, the kinetics become linear after 12 hours; the time required for extensive surface coverage as shown in Figure 27, the BSE image which shows surface coverage more clearly than the SE image in Figure 6a.

On the other hand, as shown in Figure 28, brass kinetics are linear at 30°C (dry regime) because the degree of surface coverage remains low even after 36 hours. However, brass kinetics accelerate at 40°C as shown in Figure 29, particularly in the wet regime, where surface coverage approaches 100% after 36 hours.

The kinetics for silver are essentially linear with time and very slow relative to brass and copper consistent with the minimal surface coverage even after 36 hours of exposure. An example of silver at 40°C is shown in Figure 30. Silver does not corrode as indicated by both weight-loss results and SEM observations.

The weight changes plotted above can be converted into corrosion rates. For copper, a weight change of 1mg in 24 hours on a sample with an area of $0.13dm_2$ produces a rate of 7.7mdd (milligrams per square decimeter per day) or a penetration rate (on a planar interface) of 0.03mm/year (0.0012 inches per year). Consequently, if the weight-loss data plotted in Figures 25 (30°C) and 26 (40°C) at each time are averaged, the following rates can be calculated for copper exposed to 220 ppm PH_3:

EXPOSURE TIME (hrs)	RATE at 30°C (mdd)	RATE at 30°C (mm/yr)	RATE at 40°C (mdd)	RATE at 40°C (mm/yr)
12	18	0.7	52	2
24	27	1	62	2.4
36	29	1.1	65	2.5

As noted above, increasing rates are consistent with a mechanism involving nucleation at points on the surface followed by growth with time until complete surface coverage when rates become

constant. Constant rates are reached more quickly at 40°C than at 30°C because of the faster kinetics at higher temperature.

Comments on Morphology

Nucleation and growth of surface deposits has been observed in all cases but the size of deposits varies considerably depending on whether the steady-state conditions produce wet or dry behaviour. With copper, for example, nodules approximately 50μ in diameter were observed in the dry regime (see Figure 4) but in the wet regime, large black blobs up to 1mm in diameter were formed after 36 hours(see Figure 8a). On a macroscopic scale, copper samples appeared black and shiny in the wet regime and only dulled in the dry regime.

Summary

Within the envelope of variables studied (20 to 40°C, 35 to 220 ppm PH_3, 15 to 75% RH), it is now clear that electronic equipment exposed to phosphine fumigations might fail by any of three mechanisms:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals.

The only failed electronic component examined in this laboratory was a switch supplied by Michelle Marcotte (6) in which the first possible mechanism - the build-up of non-conducting compounds rich in P and O - had occurred on the silver contacts. Reports of other failures in the field have been anecdotal and have suggested that high relative humidity was the primary factor which should be avoided - a conclusion not supported by this study.

The table below summarizes the observations made in this course of this study on metal samples from a number of sources.

METAL	SOURCE	WEIGHT GAIN	CORROSION
Copper	This study Mueller samples	Extensive	Extensive
Nickel	Mueller calculator Mueller camera	Yes	?
Brass	This study	Yes	Yes
Silver	This study Mueller fumigation	Yes	No
Stainless Steel	Mueller camera	No P signature	None found
Solder	This study Mueller calculator Mueller fumigation	No	No

It should be noted that both surface deposits and corrosion morphology were identical whether produced in this study in the laboratory or in fumigations in the field.

Conclusions

1. Within the grid of test parameters, the steady-state technique used in this study which facilitates the variation in all the parameters independently has clarified in a global sense the relative severity of metallic "corrosion" in phosphine by quantifying the extent of both surface deposit formation and metallic dissolution of the metals studied.

2. The most significant results from this study concern the identification of wet and dry regimes for copper as a function of relative humidity. Copper develops shiny black wet surface deposits only at low relative humidities (25% and lower); an observation which is both counter-intuitive and contradictory of anecdotal evidence. Dry crystalline surface deposits on copper are observed only at high relative humidities (50% and higher).

3. Different metals behave differently when exposed to phosphine in terms of wet/dry regimes and overall reaction rates. Copper, and to a lesser extent brass, develop massive wet surface coatings at low relative humidity whereas silver becomes slightly wet at high relative humidities. Copper, and to a lesser extent brass, form surface deposits and suffer pitting and general corrosion. Silver develops surface deposits but does not corrode. Solder is inert.

4. Three possible failure mechanisms for electronic equipment exposed to phospine have been identified:

- high contact resistance due to the build-up of non-conducting surface deposits
- electrical shorting due to the formation of conducting liquid phases
- disruption of circuits due to the corrosion of metals.

Recommendations

This study has made significant progress in clarifying in a global sense the relative severity of metallic "corrosion" in phosphine but the following additional work might be considered:

1. Additions to the existing data base.

   Additional work is required to define more closely the relative humidity in the range 25 to 50% at which copper changes from the wet to dry regime. This work would be done at different phosphine levels, possibly 85 and 180 ppm and even one very high level >220 ppm, to expand the data base rather than duplicate existing information. It is clear that any additional work should include replicate samples of copper for subsequent statistical analysis and nickel, a common component of circuit boards on which oxides of phosphorus have been observed after field fumigations, should be included in the study. Data at 0% carbon dioxide may be of interest to some.

2. Inducing failures in electronic equipment.

   A number of possible failure mechanisms have been identified but, with the exception of one switch with silver terminals, no failed electronic components have been examined. The experimental parameters which are believed to be most aggressive have been identified and the experimental feasibility of carrying out long-term steady state exposures has been

demonstrated. Therefore, it is now possible to induce failures in small electronic components and carry out failure analyses to identify precisely the conditions to be avoided.

3. Evaluating of the effects of cyclical exposure parameters.
   Work to date has been performed under steady-state conditions but it is possible to cycle independently the temperature, relative humidity, PH_3 concentration and CO_2 concentration to more closely duplicate the conditions of field fumigations. The effect of repeated exposures might also be of practical interest to the industry.

4. Understanding the chemistry of phosphine in contact with metals.
   The chemistry invovled in the wet/dry transition of copper exposed to phosphine is clearly not understood and is of great theoretical interest. Analytical equipment now exists which could clarify the reactions involved.

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6. Michelle Marcotte, private communication

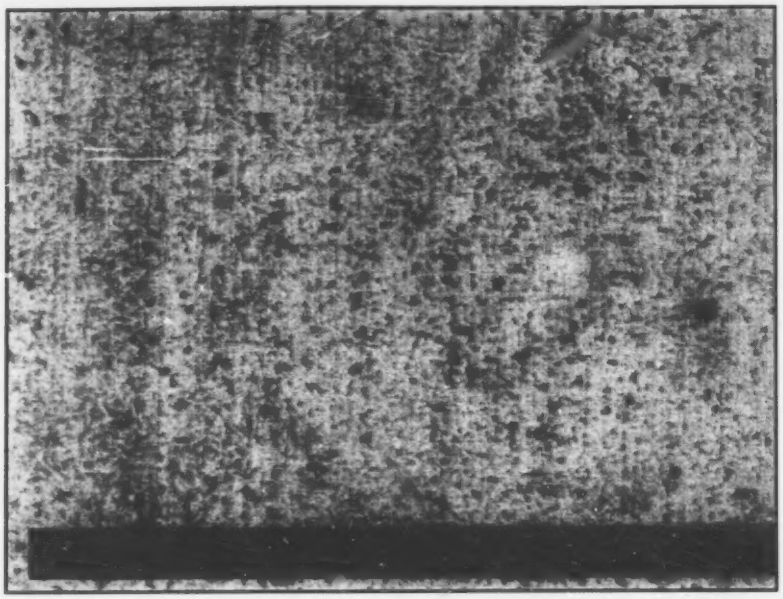

Figure 1a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

Figure 1b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 30°C and 75% RH

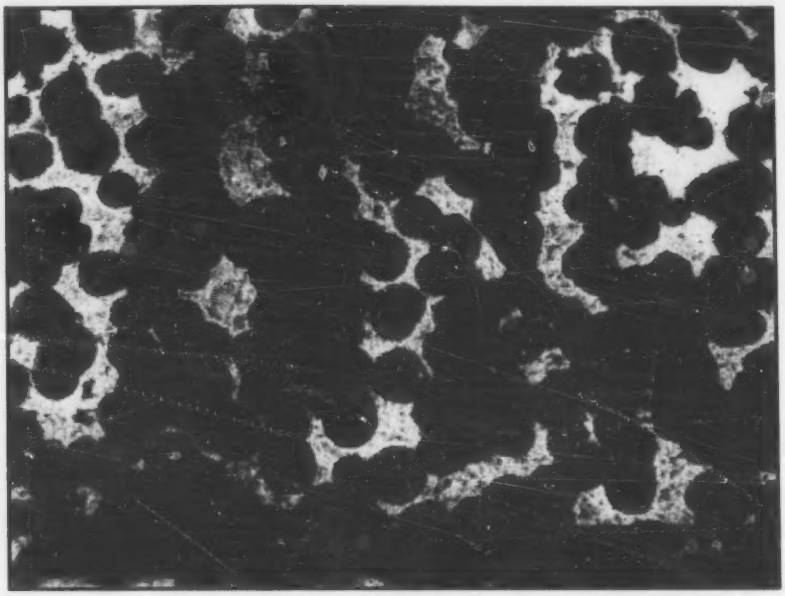

Figure 2a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

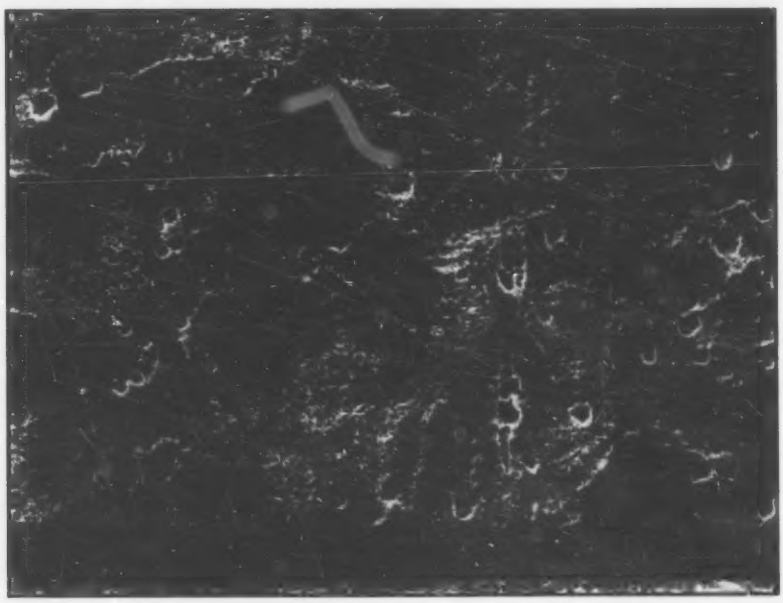

Figure 2b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 30°C and 75% RH

Figure 3a. Scanning electron micrograph (BSE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

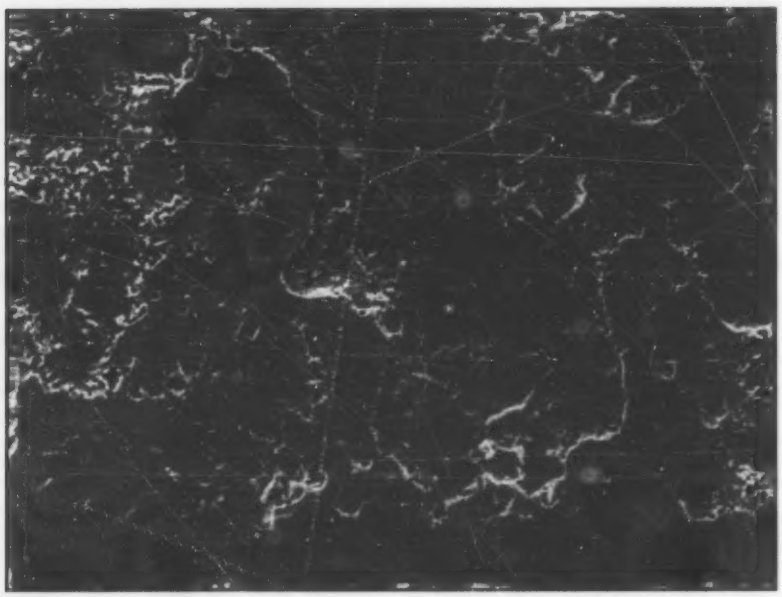

Figure 3b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

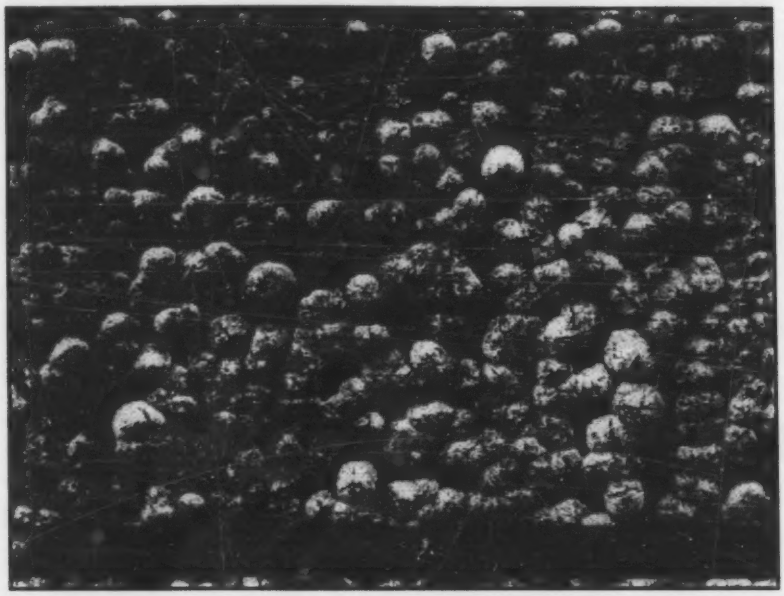

Figure 4. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 30°C and 75% RH

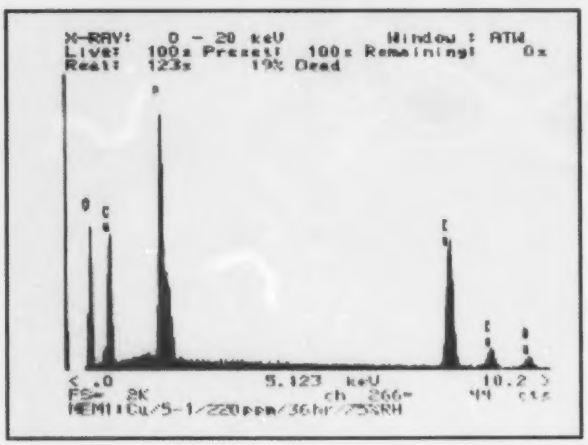

Figure 5. EDAX spectrum of the surface deposits in Figure 4.

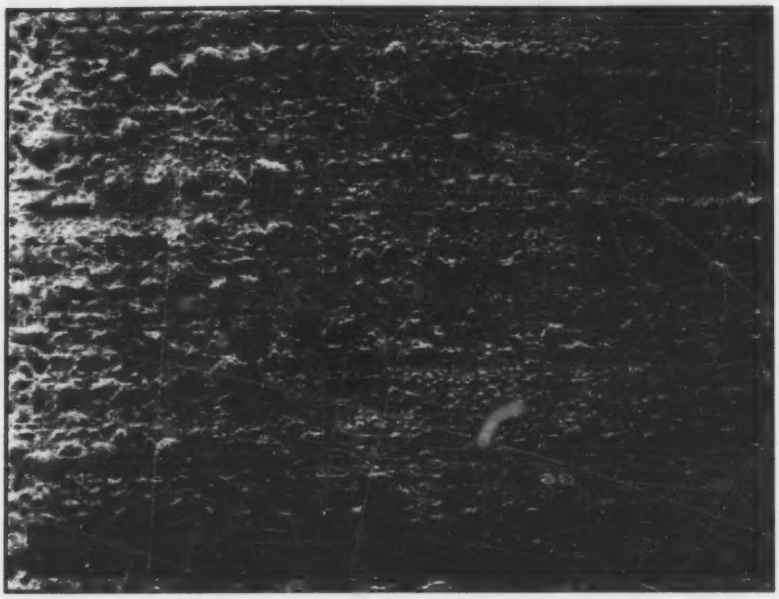

Figure 6a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 6b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

Figure 7a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

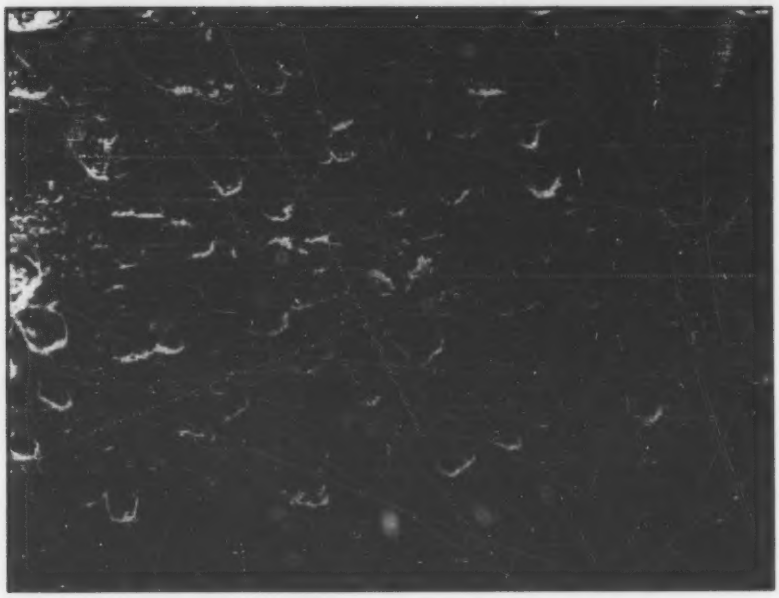

Figure 7b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 24 hours at 40°C and 15% RH

Figure 8a. Scanning electron micrograph (SE mode) of surface deposits on copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

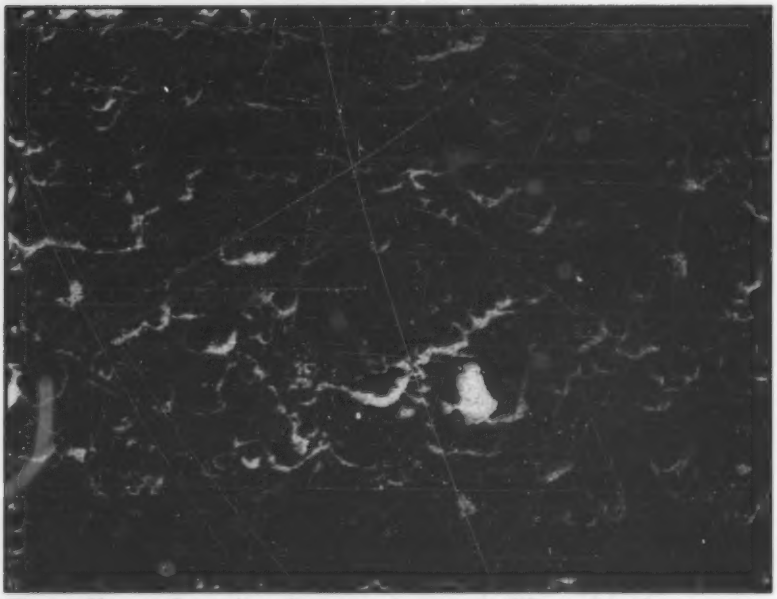

Figure 8b. Scanning electron micrograph (SE mode) of chemically cleaned copper after exposure to 220 ppm PH_3 for 36 hours at 40°C and 15% RH

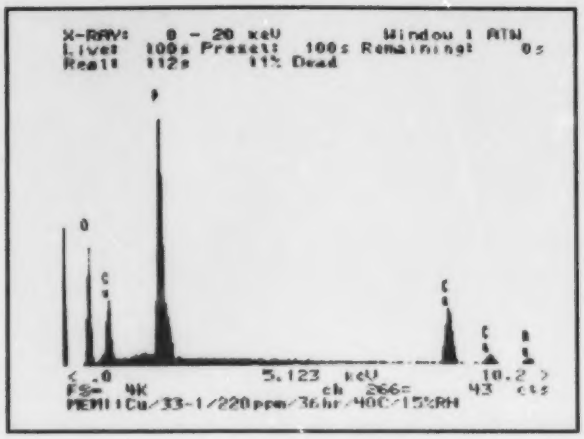

Figure 9. EDAX spectrum of the large black surface deposits in Figure 8a.

Figure 10. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 15% RH

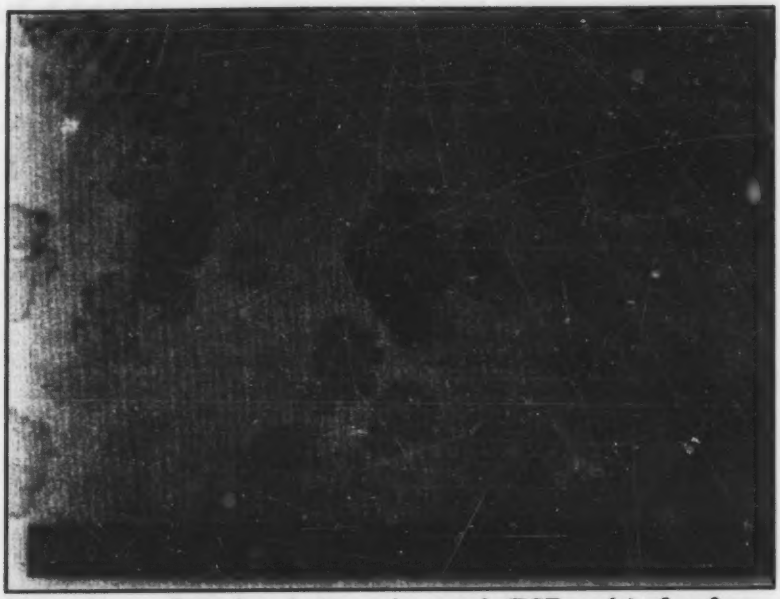

Figure 11. Scanning electron micrograph (BSE mode) of surface deposits on silver after exposure to 220 ppm PH_3 for 12 hours at 40°C and 75% RH

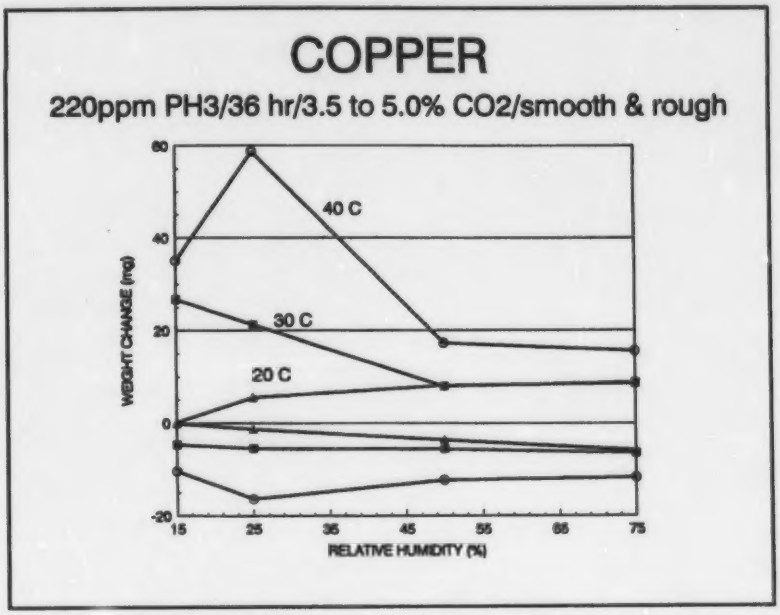

Figure 12. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

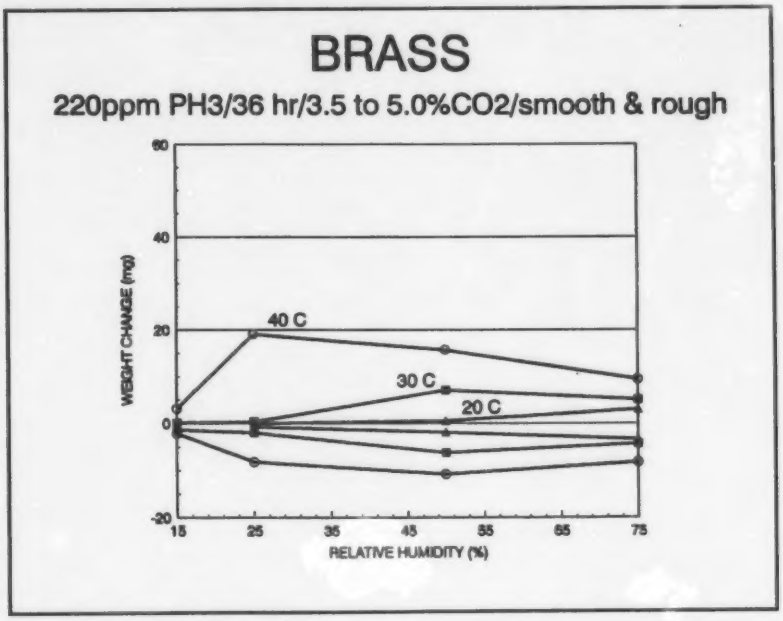

Figure 13. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

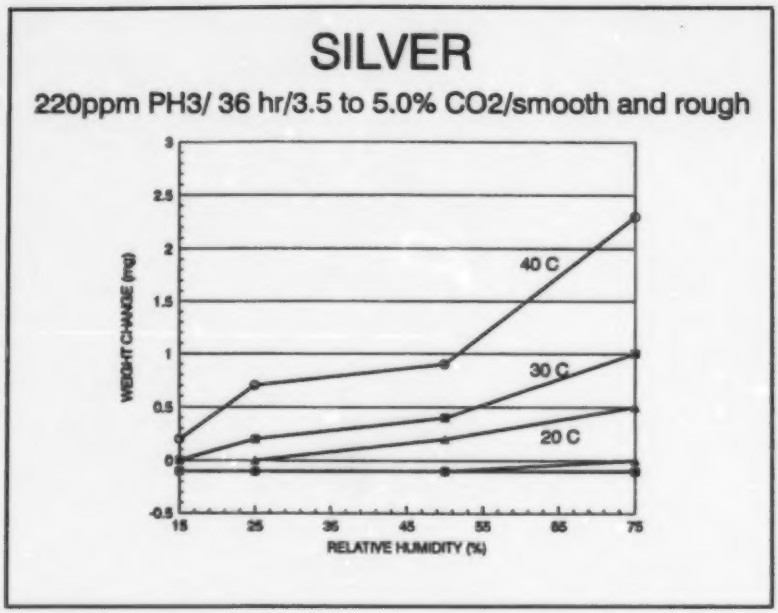

Figure 14. Effect of relative humidity on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

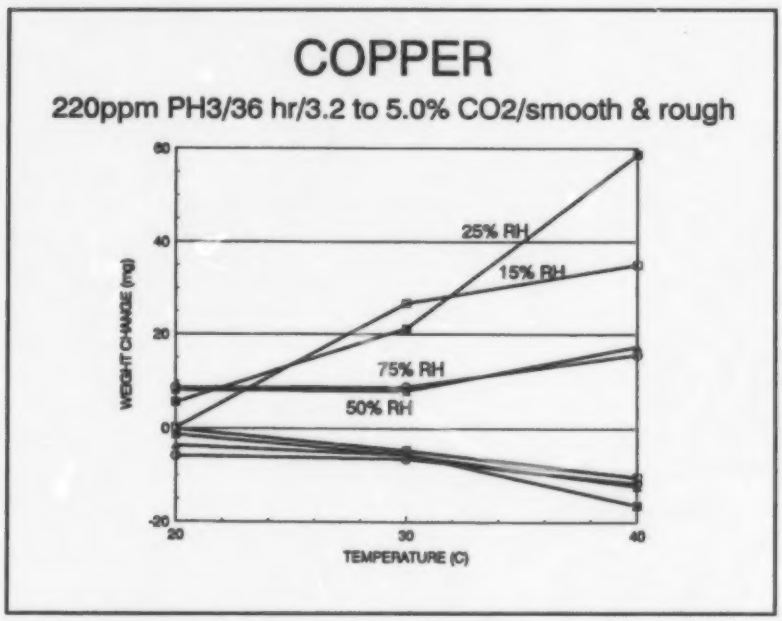

Figure 15. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

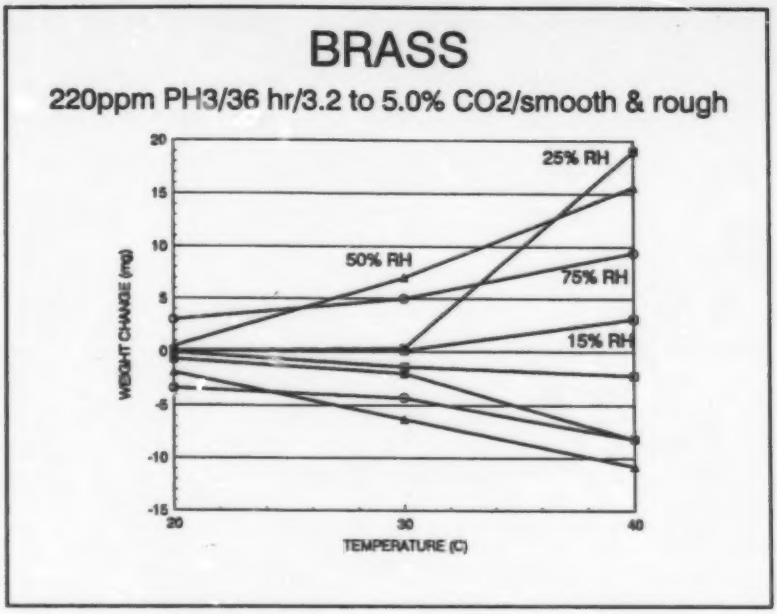

Figure 16. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

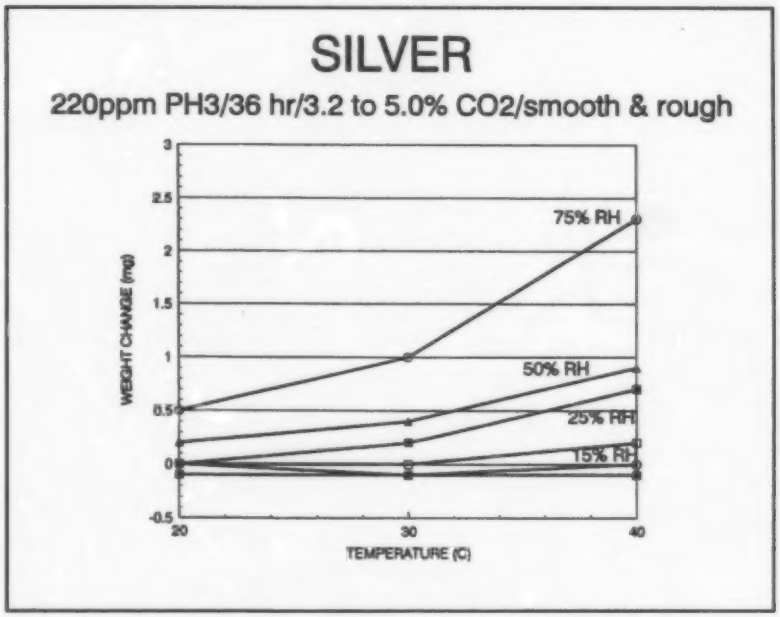

Figure 17. Effect of temperature on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

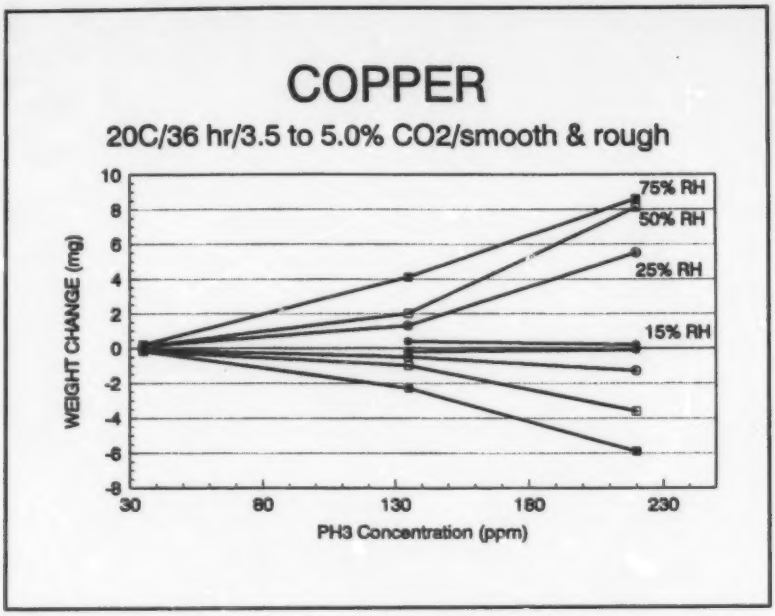

Figure 18. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

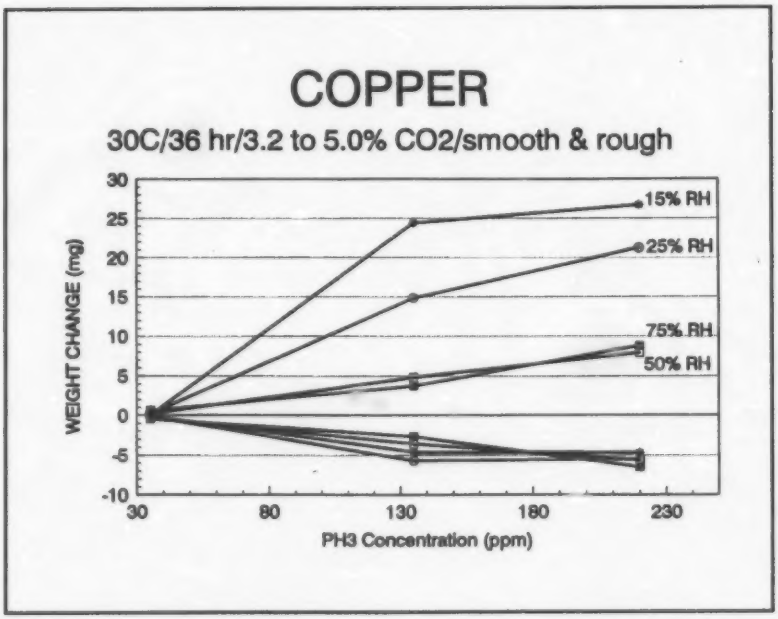

Figure 19. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

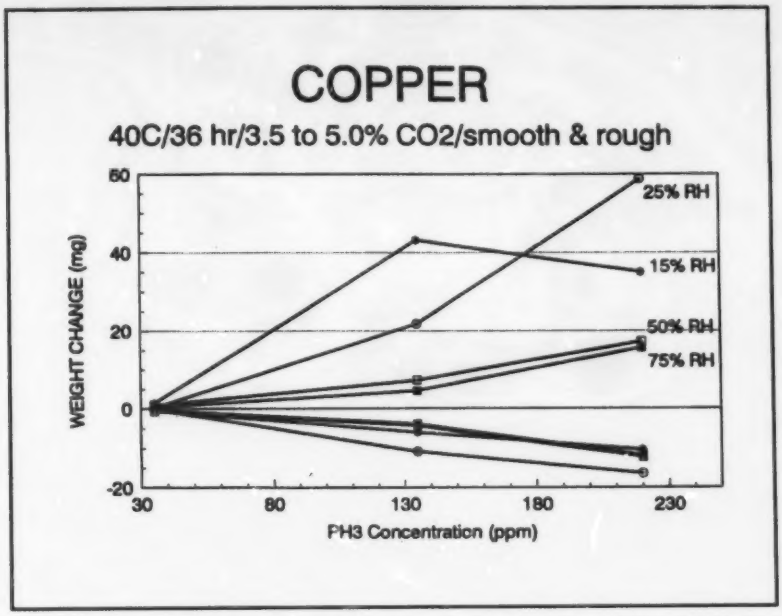

Figure 20. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

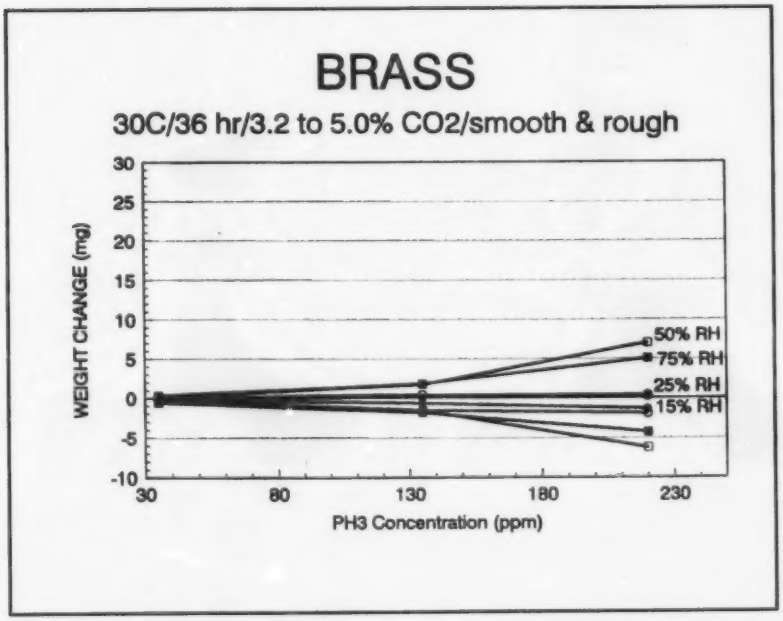

Figure 21. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

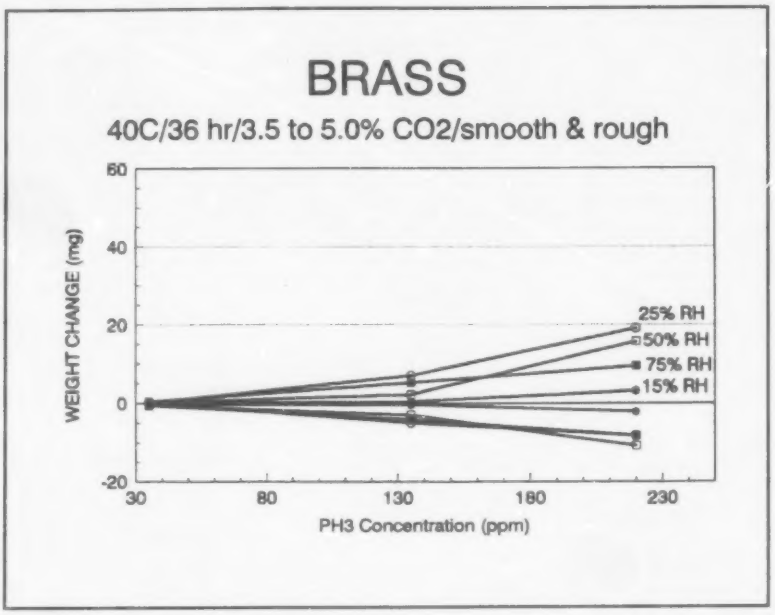

Figure 22. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

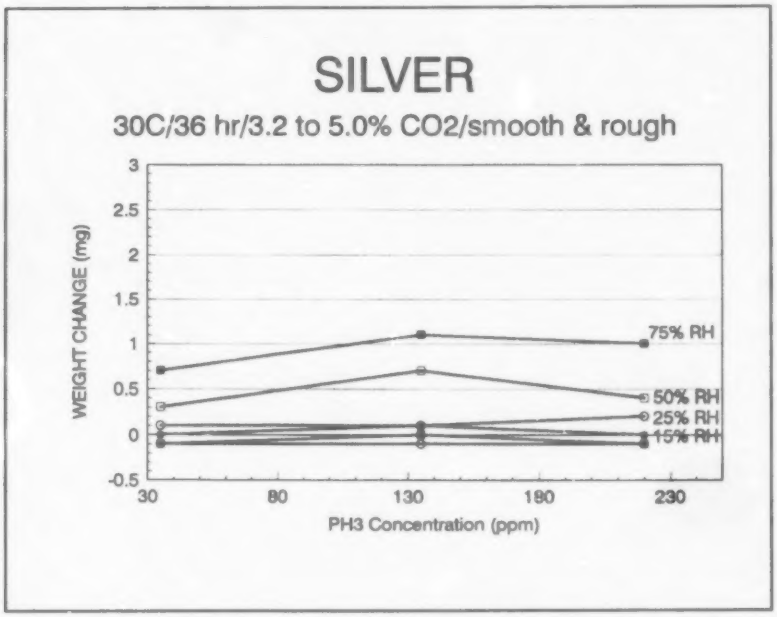

Figure 23. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

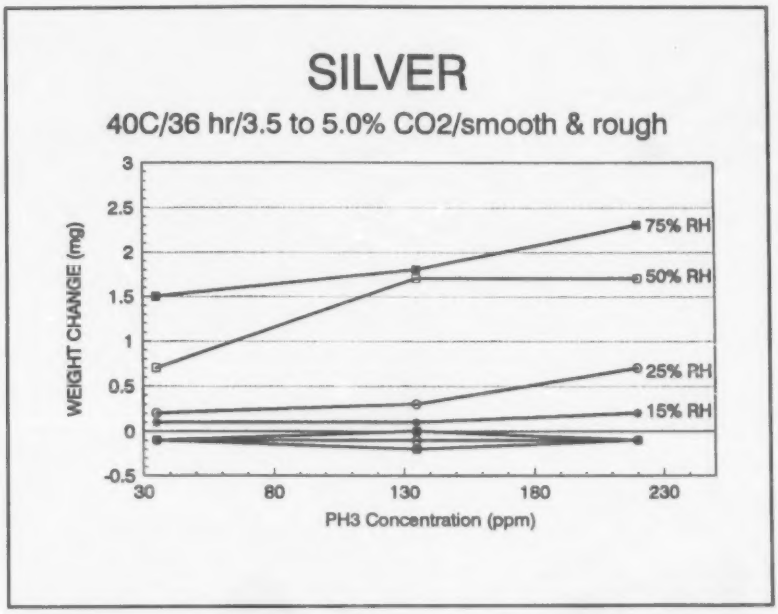

Figure 24. Effect of phosphine concentration on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

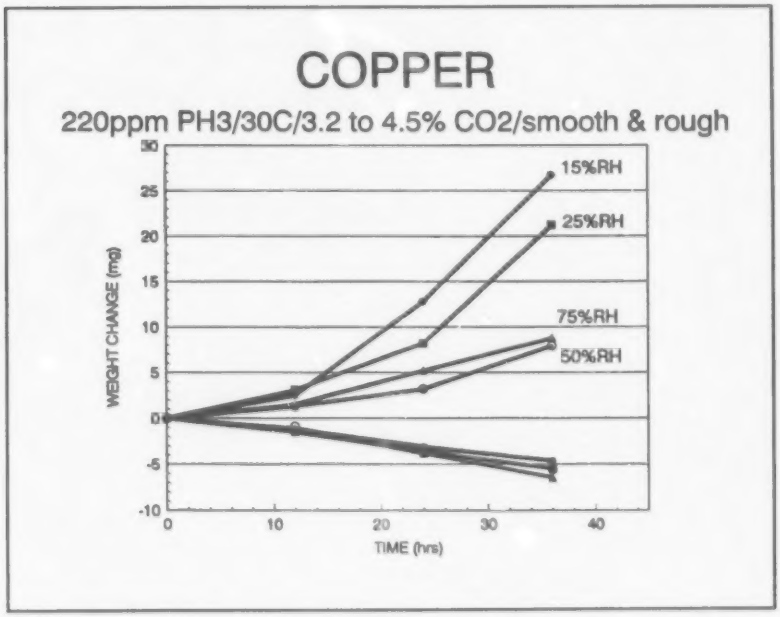

Figure 25. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

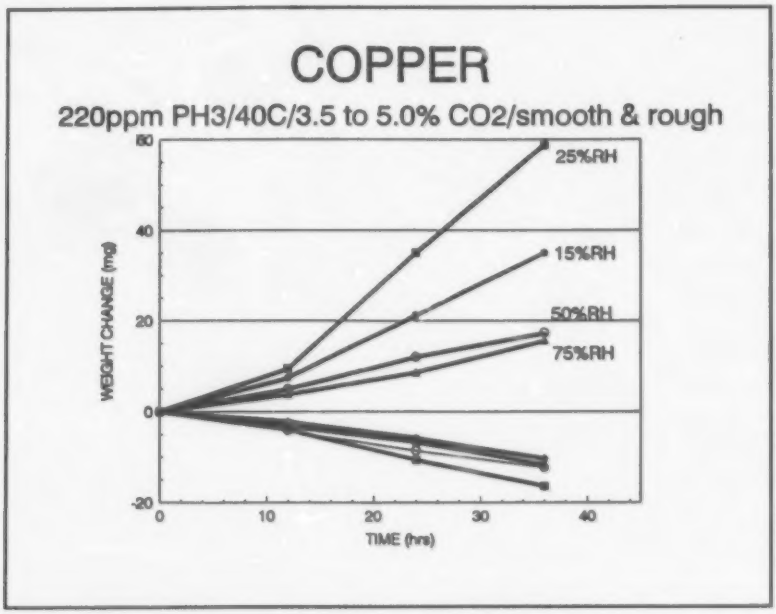

Figure 26. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of copper

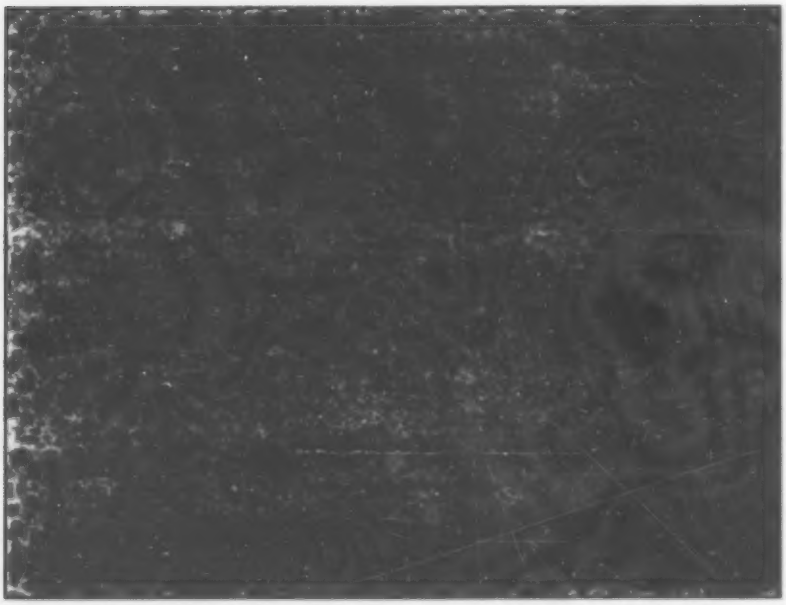

Figure 27. Scanning electron micrograph (BSE mode) showing the extent of surface coverage of copper sample in Figure 6a (SE mode)

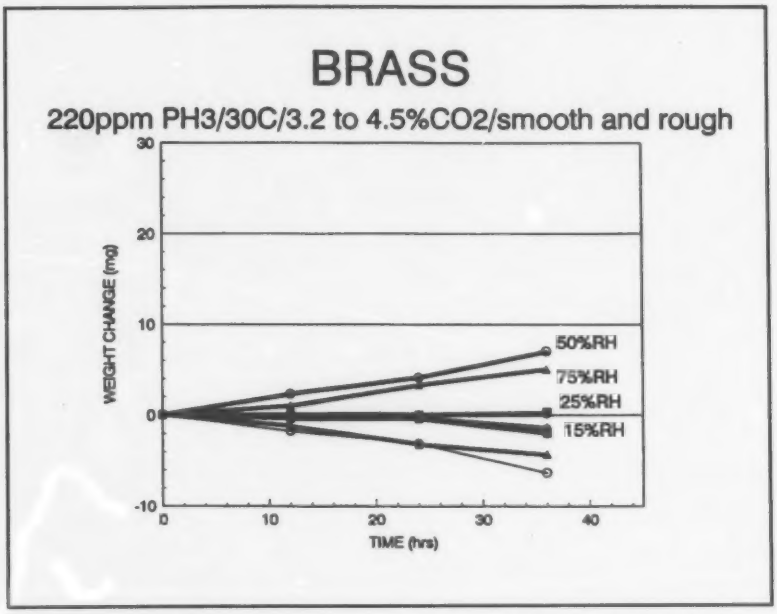

Figure 28. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

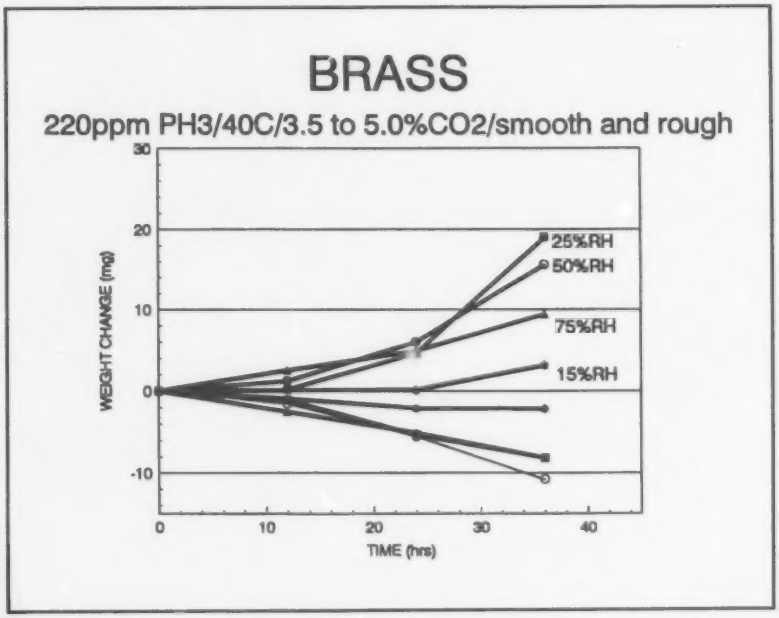

Figure 29. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of brass

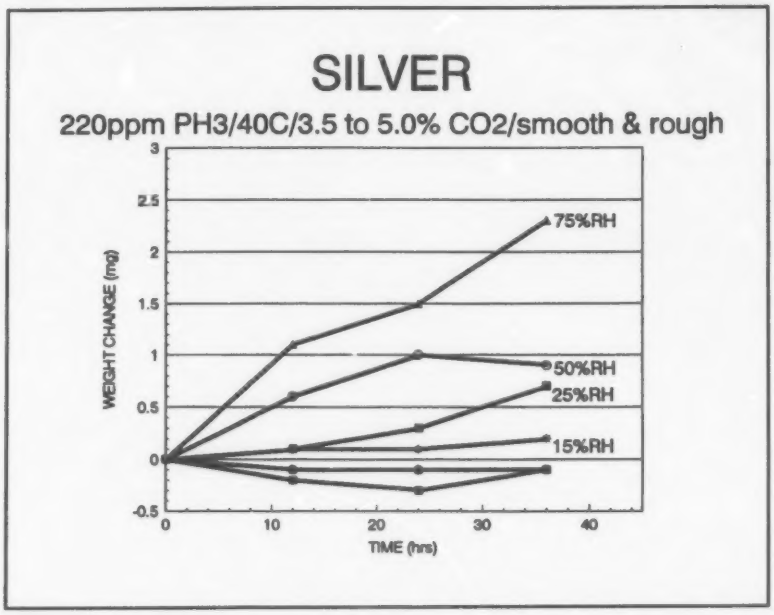

Figure 30. Effect of exposure time on weight gain (due to the deposition of oxides of phosphorus) and weight loss (due to corrosion) of silver

APPENDIX A

Tables of weight gain and weight loss are compiled in Appendix A for the following experimental parameters:

20°C, 5.0% CO_2, 35 ppm PH_3
20°C, 5.0% CO_2, 135 ppm PH_3
20°C, 3.5% CO_2, 220 ppm PH_3
20°C, 5.0% CO_2, 220 ppm PH_3

30°C, 5.0% CO_2, 35 ppm PH_3
30°C, 3.2% CO_2, 135 ppm PH_3
30°C, 5.0% CO_2, 135 ppm PH_3
30°C, 3.2% CO_2, 220 ppm PH_3
30°C, 4.5% CO_2, 220 ppm PH_3

40°C, 5.0% CO_2, 35 ppm PH_3
40°C, 5.0% CO_2, 135 ppm PH_3
40°C, 3.5% CO_2, 220 ppm PH_3
40°C, 5.0% CO_2, 220 ppm PH_3

20C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	-	-	XX	0.1	-	0.1
		24 hr	XX	-	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	-	0.2	XX	-	0.1	0.1
	Rough	12 hr	XX	-	-	-	XX	0.1	0.1	0.2
		24 hr	XX	-	-	0.1	XX	0.2	0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.2	0.2	0.2
Brass	Smooth	12 hr	XX	0.1	-	-	XX	-	0.1	0.1
		24 hr	XX	0.1	-	-	XX	-	0.1	0.2
		36 hr	XX	0.1	0.1	0.2	XX	0.1	0.1	0.2
	Rough	12 hr	XX	-	-	-	XX		0.2	0.2
		24 hr	XX	-	-	0.1	XX		0.2	0.2
		36 hr	XX	0.1	0.1	0.2	XX		0.2	0.3
Silver	Smooth	12 hr	XX	-	-	-	XX	-	-	-
		24 hr	XX	-	-	-	XX	-	-	-
		36 hr	XX	-	-	0.1	XX	-	-	-
	Rough	12 hr	XX	-	-	-	XX	0.2	0.3	0.2
		24 hr	XX	-	-	-	XX	0.2	0.2	0.2
		36 hr	XX	-	0.1	-	XX	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
All samples mounted parallel

20C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.3	0.8	-	-	0.2	0.5
		24 hr	-	0.1	0.6	2.1	-	0.1	0.3	1.4
		36 hr	0.2	0.7*	1.5	4.2	0.1	0.3	0.8	2.2
	Rough	12 hr	-	-	0.3	0.9	0.1	0.2	0.3	0.6
		24 hr	0.1	0.3	0.9	2.3	0.1	0.3	0.5	1.4
		36 hr	0.6	1.8	2.5	3.9	0.2	0.6	1.2	2.4
Brass	Smooth	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.5
		24 hr	-	-	0.1	0.7	0.1	0.1	0.3	1.0
		36 hr	-	0.1	0.4	1.2	0.1	0.3	0.8	1.9
	Rough	12 hr	-	-	-	0.2	0.2	0.2	0.3	0.5
		24 hr	-	-	-	0.3	0.2	0.3	0.3	1.0
		36 hr	-	-	0.1	0.6	0.2	0.3	0.6	1.5
Silver	Smooth	12 hr	-	-	-	-	-	-	-	-
		24 hr	-	-	-	-	-	-	-	0.1
		36 hr	-	-	0.1	0.3*	-	-	-	-
	Rough	12 hr	-	-	-	0.1	0.2	0.2	0.2	0.1
		24 hr	-	-	0.1	0.1	0.1	0.3	0.2	0.2
		36 hr	-	-	0.1	0.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

20C/220 ppm PH_3/3.5% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	XX	-	1.2	1.8	XX	-	0.7	1.3
		24 hr	XX	0.4	3.2	4.6	XX	0.1	1.7	3.3
		36 hr	XX	4.4*	6.5	6.4	XX	1.2	2.8	4.7
	Rough	12 hr	XX	0.2	2.1	2.2	XX	0.2	1.6	1.4
		24 hr	XX	0.9	4.6	5.9	XX	0.3	2.2	3.2
		36 hr	XX	7.2*	10.9	10.7	XX	1.6	4.6	6.6
Brass	Smooth	12 hr	XX	-	0.3	1.1	XX	0.1	0.3	1.0
		24 hr	XX	-	0.4	1.3	XX	0.2	0.3	2.0
		36 hr	XX	-	0.9	4.5	XX	0.8	2.0	3.9
	Rough	12 hr	XX	-	-	0.2	XX	0.2	0.4	0.7
		24 hr	XX	-	-	0.2	XX	0.3	1.3	1.3
		36 hr	XX	0.1	-	1.7	XX	0.6	2.0	2.4
Silver	Smooth	12 hr	XX	-	0.1	0.1	XX	-	-	-
		24 hr	XX	-	0.1	0.2	XX	-	-	-
		36 hr	XX	-	0.2	0.4	XX	-	-	-
	Rough	12 hr	XX	-	-	0.1	XX	0.3	0.2	0.1
		24 hr	XX	-	0.1	0.2	XX	0.2	0.2	0.1
		36 hr	XX	0.1	-	0.3	XX	0.1	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

20C/220 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.5	1.2	-	-	0.3	0.9
		24 hr	0.1	0.3	2.4	4.1	-	0.2	1.1	2.6
		36 hr	0.2	4.4*	6.1	5.1	-	1.1	3.1	5.1
	Rough	12 hr	0.1	0.1	0.6	1.7	0.1	0.1	0.4	1.0
		24 hr	0.1	0.6	4.1	6.7	0.1	0.2	1.6	3.9
		36 hr	0.2	6.1*	8.9	12.0	0.1	1.2	4.0	7.0
Brass	Smooth	12 hr	-	0.1	-	0.7	-	-	0.2	0.8
		24 hr	-	-	0.1	1.7	-	0.1	0.8	2.2
		36 hr	0.1	-	1.1	4.5	-	0.8	2.0	4.3
	Rough	12 hr	-	-	-	0.4	0.2	0.2	0.4	0.8
		24 hr	-	-	-	0.2	0.2	0.2	0.9	1.3
		36 hr	-	-	0.1	1.4	0.2	0.7	1.6	2.8
Silver	Smooth	12 hr	-	-	-	0.1	-	-	0.1	0.1
		24 hr	-	-	0.3*	0.2	-	-	-	-
		36 hr	-	-	0.4*	0.6	-	-	-	-
	Rough	12 hr	-	-	0.3	0.3	0.2	0.3	0.1	0.2
		24 hr	-	-	0.1	-	0.2	0.2	0.2	0.3
		36 hr	-	-	0.2	0.7	0.2	0.3	-	-

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	-	-	0.2	0.1	0.1	0.1	0.1
		24 hr	-	-	0.2	0.2	-	0.1	0.2	0.2
		36 hr	-	0.1	0.3	0.6	-	0.1	0.3	0.5
	Rough	12 hr	-	-	-	0.2	0.1	0.1	0.2	0.3
		24 hr	-	0.2	0.2	0.2	0.2	0.1	0.1	0.2
		36 hr	0.1	0.2	0.1	0.5	0.1	0.2	0.3	0.5
Brass	Smooth	12 hr	-	-	-	0.1	-	0.1	0.2	0.3
		24 hr	-	0.1	0.1	0.3	0.1	-	0.2	0.3
		36 hr	-	0.1	0.2	0.3	0.1	0.1	0.2	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.2	0.3
		24 hr	-	-	-	0.2	0.1	0.2	0.2	0.3
		36 hr	-	-	0.2	0.3	0.1	0.2	0.3	0.6
Silver	Smooth	12 hr	-	-	-	0.1	-	0.1	0.1	-
		24 hr	-	-	0.3	0.5	-	-	-	-
		36 hr	-	0.1	0.4	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.1	0.1	0.1	0.2	0.1
		24 hr	-	-	0.2	0.6	0.1	0.2	0.2	-
		36 hr	-	0.1	0.2	0.6	0.1	0.2	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/135 ppm PH_3/3.2% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	-	0.1	0.4	1.0	-	0.1	0.4	0.9
		24 hr	2.4*	3.3*	1.2	1.1	0.8	1.0	1.0	1.0
		36 hr	21.2*	16.0*	2.9	2.8	4.2	6.4	1.8	1.8
	Rough	12 hr	0.3*	0.4*	0.6	0.9	0.3	0.4	0.5	0.7
		24 hr	3.9*	3.5*	2.4	2.1	1.2	1.7	1.6	0.5
		36 hr	27.3*	16.2*	4.9	3.4	4.0	7.7	3.6	2.8
Brass	Smooth	12 hr	0.1	-	0.7	0.5	-	0.2	0.6	0.6
		24 hr	-	-	1.6	0.9	0.4	0.6	1.2	0.7
		36 hr	0.1	0.3	3.0	2.0	1.0	0.5	2.0	1.8
	Rough	12 hr	-	-	0.5	0.4	-	0.3	0.5	0.4
		24 hr	0.1	0.1	0.5	0.5	0.3	0.7	0.9	0.8
		36 hr	0.1	-	1.6	1.7	1.4	1.1	1.6	1.8
Silver	Smooth	12 hr	-	0.1	0.1	0.3	-	-	-	-
		24 hr	-	-	0.1	0.2	-	-	-	0.1
		36 hr	0.1	-	0.9	0.7	-	-	-	-
	Rough	12 hr	-	-	0.1	0.3	0.1	0.2	0.1	0.1
		24 hr	-	0.1	0.2	0.6	0.1	0.1	0.1	0.1
		36 hr	0.1	0.1	0.7	1.0	-	0.1	-	-

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	0.3	0.8	1.2	-	0.2	0.4	0.7
		24 hr	2.9*	3.4*	2.3	3.3	1.3	1.0	0.9	1.8
		36 hr	23.3*	13.8*	5.1	4.5	4.8	4.2	4.6	3.6
	Rough	12 hr	0.1*	0.7*	1.1	1.1	0.2	0.4	0.8	0.9
		24 hr	5.6*	4.5*	3.3	2.4	1.9	1.6	2.1	1.6
		36 hr	26.0*	13.3*	6.1	3.9	5.2	4.5	4.2	2.6
Brass	Smooth	12 hr	-	0.1	0.9	1.1	0.1	0.2	0.6	0.9
		24 hr	-	0.1	0.8	1.2	0.1	0.7	0.8	1.6
		36 hr	-	0.9	1.5	1.6	0.1	3.1	1.6	1.6
	Rough	12 hr	-	0.1	0.4	0.9	0.2	0.2	0.6	0.9
		24 hr	-	-	0.4	0.9	0.1	0.7	1.4	1.5
		36 hr	-	0.3	0.8	1.9	0.2	1.6	1.2	2.2
Silver	Smooth	12 hr	-	-	0.1	0.4	-	-	-	-
		24 hr	-	-	0.5	0.6	-	-	-	-
		36 hr	0.1	0.1	0.4	1.4	-	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	-	-	0.1	0.1
		24 hr	-	0.1	0.1	0.7	0.1	-	0.1	-
		36 hr	0.1	0.1	0.7	1.2	0.1	-	0.1	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

30C/220 ppm PH_3/3.2%CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	1.2*	1.2	0.9	0.1	0.5	1.0	0.7
		24 hr	2.9*	8.2*	2.8	1.9	0.7	3.6	2.8	1.6
		36 hr	31.6*	23.4*	7.8	5.3	4.2	5.6	6.0	4.3
	Rough	12 hr	1.2*	1.8*	1.8	1.3	0.3	0.8	1.1	1.0
		24 hr	2.0*	8.6*	7.8	3.7	0.6	2.4	5.0	2.7
		36 hr	21.9*	13.8*	8.9	6.3	3.7	4.4	6.7	4.8
Brass	Smooth	12 hr	0.1	-	3.1	0.9	0.1	0.4	3.1	0.9
		24 hr	0.1	-	6.5	2.7	0.2	0.6	6.5	2.3
		36 hr	0.2	0.9	20.4	9.3	1.8	2.1	10.7	5.9
	Rough	12 hr	0.1	-	1.5	1.0	0.2	0.5	1.4	1.2
		24 hr	-	-	0.9	2.3	0.5	0.7	1.5	2.4
		36 hr	-	0.1	7.4	4.4	1.7	1.7	5.1	3.9
Silver	Smooth	12 hr	0.1	-	0.1	0.1	-	0.1	-	-
		24 hr	0.1	0.1	0.1	0.7	0.1	-	-	-
		36 hr	-	0.1	0.6	1.3	0.1	-	-	-
	Rough	12 hr	-	0.1	0.1	0.4	0.2	0.1	0.2	0.1
		24 hr	-	-	0.2	0.9	0.1	0.2	-	0.1
		36 hr	-	0.3	0.4	1.3	0.2	0.2	0.1	-

The solder samples gained no weight under these test conditions
*Samples were wet
25 & 50% RH - samples mounted parallel
15 & 75% RH - samples mounted radially

30C/220 ppm PH_3/4.5% CO_2

Sample Area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	1.6	1.3	0.9	1.9	0.8	1.1	0.5	1.4
		24 hr	27.9*	9.0*	2.3	6.0	6.8	4.2	2.2	4.9
		36 hr	21.2*	13.5*	5.0	11.1	4.8	4.7	3.6	8.9
	Rough	12 hr	6.9*	8.2*	1.4	2.0	3.4	3.7	1.0	1.6
		24 hr	18.3*	6.8*	5.0	9.3	4.1	4.1	3.1	5.9
		36 hr	31.9*	34.0*	9.9	12.6	6.1	7.4	5.9	8.1
Brass	Smooth	12 hr	-	0.2	3.8	1.0	-	0.6	1.4	1.2
		24 hr	-	-	7.4	6.9	-	-	2.9	4.8
		36 hr	-	0.3	14.7	5.5	1.0	3.8	6.6	4.3
	Rough	12 hr	-	-	0.8	1.1	0.4	0.2	0.7	1.6
		24 hr	-	-	1.5	1.4	0.5	0.2	1.3	3.4
		36 hr	-	-	1.9	0.9	1.2	0.2	2.8	3.2
Silver	Smooth	12 hr	-	-	0.4	0.1	-	0.2	-	-
		24 hr	-	-	0.3	0.2	-	-	-	0.1
		36 hr	-	0.1	0.4	0.8	-	-	0.1	0.1
	Rough	12 hr	-	-	0.2	0.3	-	0.5	0.3	0.1
		24 hr	-	-	0.3	0.3	-	-	-	0.1
		36 hr	-	0.1	0.3	0.6	-	0.1	0.1	0.2

The solder samples gained no weight under these test conditions

* Samples were wet

All samples mounted radially

40C/35 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	0.1	-	0.1	0.2	-	0.1	0.1	0.1
		24 hr	0.2	-	0.5	0.3	0.1	-	0.4	0.1
		36 hr	0.3	0.1	0.7	0.4	0.2	-	0.5	0.3
	Rough	12 hr	0.1	0.1	0.1	0.2	0.2	0.1	0.2	0.2
		24 hr	0.4*?	0.1	0.4	0.3	0.2	0.1	0.5	0.2
		36 hr	2.4*	0.3	1.1	0.4	1.0	0.3	0.8	0.4
Brass	Smooth	12 hr	-	-	0.1	0.2	0.1	-	0.1	0.3
		24 hr	-	-	0.3	0.4	0.1	-	0.3	0.2
		36 hr	0.1	0.2	0.3	0.5	0.2	-	0.4	0.5
	Rough	12 hr	-	-	-	0.1	0.1	0.1	0.3	0.2
		24 hr	-	-	0.1	0.2	0.2	-	0.5	0.4
		36 hr	-	-	0.1	0.3	0.3	0.1	0.5	0.6
Silver	Smooth	12 hr	-	-	0.2	0.2	-	-	-	-
		24 hr	-	-	0.6	0.6*	-	-	-	-
		36 hr	-	-	0.2	1.3*	-	-	-	-
	Rough	12 hr	0.1	-	0.4	0.6	-	0.1	0.2	0.1
		24 hr	-	0.2	0.7	1.3	0.2	0.1	0.2	0.1
		36 hr	0.2	0.3	1.1	1.6	0.1	0.1	0.2	0.1

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel

40C/135 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25%+ RH	50% RH	75% RH	15% RH	25%+ RH	50% RH	75% RH
Copper	Smooth	12 hr	-	1.0	1.6	1.2	0.1	0.7	1.2	1.0
		24 hr	8.4*	4.5	3.8	2.4	2.1	1.7	2.7	2.3
		36 hr	40.9*	19.1	5.9	5.0	5.9	7.9	3.2	4.1
	Rough	12 hr	1.7*	3.7	2.3	1.2	0.6	1.7	1.9	1.0
		24 hr	22.6*	13.8	5.3	2.2	3.7	9.0	3.6	1.9
		36 hr	45.2*	24.5	8.6	4.1	6.0	13.8	5.5	3.6
Brass	Smooth	12 hr	-	0.3	0.6	0.7	0.2	0.6	0.7	0.9
		24 hr	0.1	1.7	1.5	2.2	0.4	1.6	2.3	2.3
		36 hr	0.7	11.9*	3.2	4.7	0.4	6.1	3.7	3.8
	Rough	12 hr	-	-	0.2	0.8	0.4	0.9	0.8	0.9
		24 hr	-	-	0.4	1.6	0.2	1.5	1.1	1.7
		36 hr	-	2.1	1.2	5.6	0.4	3.9	2.3	4.4
Silver	Smooth	12 hr	-	-	0.3	0.7*	-	-	-	-
		24 hr	0.4	0.1	0.4	1.3*	-	-	-	0.1
		36 hr	-	0.3	1.3	2.0*	-	-	-	-
	Rough	12 hr	-	0.1	0.6	1.0	0.4	0.3	0.2	0.2
		24 hr	0.1	0.1	1.1	1.3	0.3	0.4	0.2	0.2
		36 hr	0.1	0.3	2.0	1.5	0.2	0.2	0.2	0.1

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel
+A power failure near the end of the experiment turned off the PH^3 and caused the humidity to rise. The copper samples had obviously been wet during the experiment but were dry when removed.

40C/220 ppm PH_3/3.5% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.2*	7.4*	4.5	3.5	2.0	2.9	3.6	2.4
		24 hr	19.8*	29.3*	10.5	7.4	6.2	10.2	7.6	5.4
		36 hr	37.7*	64.0*	17.6	11.9	10.6	18.7	12.3	11.1
	Rough	12 hr	9.0*	12.9*	5.7	4.0	2.2	5.3	4.4	3.2
		24 hr	22.8*	36.6*	15.7	9.9	4.7	11.0	9.3	6.0
		36 hr	34.6*	62.4*	19.8	18.8	11.9	16.4	12.0	12.2
Brass	Smooth	12 hr	0.1	0.2	1.5	3.2	1.1	0.9	1.1	2.4
		24 hr	0.2	2.2	4.2	2.8	2.9	5.7	5.0	4.4
		36 hr	1.2*?	25.6*	9.9	6.7	0.3	12.1	9.8	7.3
	Rough	12 hr	0.1	0.1	0.2	1.3	0.9	1.7	1.2	2.2
		24 hr	-	-	2.3	2.0	1.8	3.8	3.5	3.5
		36 hr	-	2.1	5.4	7.7	0.2	1.6	6.0	6.0
Silver	Smooth	12 hr	0.1	-	0.4*	0.8*	-	-	-	-
		24 hr	0.1	-	0.8*	1.2*	-	0.1	-	-
		36 hr	0.2	0.3	1.1*	1.6*	-	-	-	-
	Rough	12 hr	0.1	0.1	0.3	0.8	0.2	0.4	0.2	0.3
		24 hr	0.1	-	0.5	1.3	0.2	0.3	0.2	0.2
		36 hr	0.1	0.2	1.0	2.4	0.2	0.2	0.2	0.2

The solder samples gained no weight under these test conditions
*Samples were wet
All samples mounted parallel

40C/220 ppm PH_3/5.0% CO_2

Sample area = 0.13 dm^2			Weight Gain (mg)				Weight Loss (mg)			
			15% RH	25% RH	50% RH	75% RH	15% RH	25% RH	50% RH	75% RH
Copper	Smooth	12 hr	6.5*	6.0*	4.0	4.2	2.1	2.6	3.6	4.4
		24 hr	20.1*	33.7*	8.9	8.5	6.1	8.6	8.0	7.3
		36 hr	34.6*	55.7*	13.4	16.9	9.4	15.1	11.8	11.6
	Rough	12 hr	8.2*	11.2*	5.9	3.5	2.6	5.1	5.1	2.9
		24 hr	21.9*	40.3*	12.7	8.7	6.1	13.1	9.3	8.1
		36 hr	33.4*	52.6*	18.3	14.6	9.5	15.4	13.1	11.8
Brass	Smooth	12 hr	0.1	0.4	2.4	3.5	1.3	0.6	2.1	3.0
		24 hr	-	14.3*	14.8	10.1	1.7	7.4	10.2	8.2
		36 hr	11.1*	31.2*	32.4	16.7	6.4	11.5	16.9	11.5
	Rough	12 hr	-	0.1	0.5	2.0	0.3	1.2	1.4	2.5
		24 hr	-	1.8	2.8	4.6	1.9	4.4	3.3	4.3
		36 hr	0.1	16.9*	14.8	6.5	1.9	7.4	10.5	7.8
Silver	Smooth	12 hr	-	0.2	0.7*	1.4	-	0.1	-	-
		24 hr	0.2	1.1*	1.1*	1.5*	-	0.1	-	-
		36 hr	-	1.4*	2.2*	2.7*	-	-	-	-
	Rough	12 hr	-	0.2	0.9	1.3	0.5	0.4	0.2	0.3
		24 hr	0.1	0.2	1.4	1.8	0.5	0.5	0.2	0.1
		36 hr	0.3	0.9	2.3	2.5	0.3	0.2	0.3	-

The solder samples gained no weight under these test conditions

*Samples were wet

All samples mounted parallel